PB81-136186

Analytical Procedures for Characterizing Unregulated Emissions from Vehicles Using Middle-Distillate Fuels

Southwest Research Inst.
San Antonio, TX

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Apr 80

U.S. Department of Commerce
National Technical Information Service
NTIS

PB81-136186

Analytical Procedures for Characterizing Unregulated Emissions from Vehicles Using Middle-Distillate Fuels

Southwest Research Inst.
San Antonio, TX

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Apr 80

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-80-068
April 1980

PB81-136186

Research and Development

EPA

Analytical Procedures for Characterizing Unregulated Emissions from Vehicles Using Middle-Distillate Fuels

Interim Report

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-80-068

2.

3. RECIPIENT'S ACCESSION NO. PB81 136186

4. TITLE AND SUBTITLE
ANALYTICAL PROCEDURES FOR CHARACTERIZING UNREGULATED EMISSIONS FROM VEHICLES USING MIDDLE-DISTILLATE FUELS
Interim Report

5. REPORT DATE April 1980

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Lawrence R. Smith, Mary E. Parness, E. Robert Fanick, and Harry E. Dietzmann

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78284

10. PROGRAM ELEMENT NO. 07A1D 14-0457 (FY-80)

11. CONTRACT/GRANT NO. 68-02-2497

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Sciences Research Laboratory - RTP, NC
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

13. TYPE OF REPORT AND PERIOD COVERED Interim

14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This research program was initiated with the objective of developing, codifying and testing a group of chemical analytical methods for measuring toxic compounds in the exhaust of distillate-fueled engines (i.e. diesel, gas turbine, Stirling, or Rankin cycle powerplants). It is a part of a larger effort to characterize these components from a number of prototype powerplants and, thus, represents a logical first step in the process.

Methods of collection and analysis for aldehydes and ketones, for hydrogen cyanide and cyanogen, for hydrogen sulfide, carbonyl sulfide and organic sulfides, for ammonia and amines, for nitrous oxide, sulfur dioxide, individual hydrocarbons, for soluble sulfate and N-nitrosodimethylamine, benzo-a-pyrene, and phenols were studied in detail. Ten analytical procedures were developed and codified. Interference studies and proof-tests in diesel engine exhaust were conducted with every procedure and the results of these experiments are reported in detail.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Vehicles * Distillates * Fuels * Emission * Collecting methods * Chemical analysis		13B 11G 14B 21D

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)* UNCLASSIFIED

20. SECURITY CLASS *(This page)* UNCLASSIFIED

21. NO. OF PAGES

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-600/2-80-068
April 1980

ANALYTICAL PROCEDURES FOR CHARACTERIZING UNREGULATED EMISSIONS FROM VEHICLES USING MIDDLE-DISTILLATE FUELS

Interim Report

by

Lawrence Smith
Mary Ann Parness
E. Robert Fanick
Harry E. Dietzmann

Southwest Research Institute
San Antonio, Texas 78284

Contract No. 68-02-2497

Project Officer

Ronald L. Bradow
Emissions Measurement and Characterization Division
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWARD

The Clean Air Act as amended in 1977 requires manufacturers of automobiles to certify that the emissions of automobiles represent no unreasonable risk to the public health and safety. EPA's role in enforcing this section of the Act has been to formulate methods and procedures by which toxic pollutants which might be emitted from various kinds of automobile engines could be measured and assessed. The Environmental Sciences Research Laboratory contributes to this overall agency effort through programs engaged in

studies to identify and measure toxic pollutants in source emissions and in the ambient air.

development of methods and procedures to measure air pollutants

development of modeling procedures which permit prediction of ambient air quality impacts from source emissions data.

This report is the second of two similar documents relating the development of analytical methods for measuring trace toxic pollutants in mobile source exhaust gas. The first of these reports provided fully tested procedures for 10 toxic gases in the exhaust of gasoline engines. The current report deals with many of the same compounds and methods now fully qualified for use with distillate-fueled engines such as diesel or gas-turbine powerplants. It is intended that this report serve as a working guide to the automotive industry and to a variety of government and academic research institutions, providing well-tested analytical methods for studying hazardous pollutant emissions from automotive powerplants.

A.H. Ellison
Director
Environmental Sciences Research Laboratory

ABSTRACT

This research program was initiated with the objective of developing, codifying and testing a group of chemical analytical methods for measuring toxic compounds in the exhaust of distillate-fueled engines (i.e. diesel, gas turbine, Stirling, or Rankin cycle powerplants). It is a part of a larger effort to characterize these components from a number of prototype powerplants and, thus, represents a logical first step in the process.

Methods of collection and analysis for aldehydes and ketones, for hydrogen cyanide and cyanogen, for hydrogen sulfide, carbonyl sulfide and organic sulfides, for ammonia and amines, for nitrous oxide, sulfur dioxide, individual hydrocarbons, for soluble sulfate and N-nitrosodimethylamine, benzo-a-pyrene, and phenols were studied in detail. Ten analytical procedures were developed and codified. Interference studies and proof-tests in diesel engine exhaust were conducted with every procedure and the results of these experiments are reported in detail.

All of the procedures were found to be suitable for use in exhaust emissions characterization studies. The sampling parameters were found to be adequate for the collection of trace levels of exhaust components using standard CVS sampling techniques. Interferences were, in general, minimal although there were two significant problem areas. Phthalate ester interferes with crotonaldehyde determinations and this contaminant must be avoided in the procedure. In the hydrogen sulfide method, SO2 decreases the apparent sulfide, and its presence must be corrected for. While other interferences were noted, all could be avoided with the appropriate precautions noted in the final procedure.

Qualification tests were conducted by introducing known quantities of these pollutants into the exhaust of a diesel engine operating on a standard emissions test CVS tunnel. The results of these experiments indicated completely quantitative recovery for aldehydes and ketones, SO2, nitrous oxide, total cyanide and phenols. Hydrogen sulfide is lost to the extent of ten percent at normal exhaust levels. Amines, ammonia and organic sulfides can be lost in sampling in significant amounts in the CVS apparatus. These losses must be taken into account when calculating exhaust contributions.

CONTENTS

Foreword iii
Abstract iv
Figures. vi
Tables x

1. Introduction 1
2. Aldehyde and Ketone Procedure. 3
3. Total Cyanide Procedure. 20
4. Individual Hydrocarbon Procedure 43
5. Organic Amine Procedure. 53
6. Sulfur Dioxide Procedure 74
7. Nitrous Oxide Procedure. 89
8. Hydrogen Sulfide Procedure 98
9. Ammonia Procedure. 112
10. Organic Sulfide Procedure. 127
11. Phenol Procedure 158
12. The Qualification Experiment 178
13. Results and Conclusions. 184

References 187

Appendices

A. Aldehyde and Ketone Procedure. 197
B. Total Cyanide Procedure. 227
C. Individual Hydrocarbon Procedure 251
D. Organic Amine Procefure. 273
E. Sulfur Dioxide Procedure 294
F. Nitrous Oxide Procedure. 317
G. Hydrogen Sulfide Procedure 334
H. Ammonia Procedure. 359
I. Organic Sulfide Procedure. 382
J. Phenol Procedure 415
K. Sulfate Procedure. 440
L. DMNA Sampling Procedure. 460
M. DMNA Analysis Procedure. 470
N. BaP Sampling and Analysis. 484

FIGURES

Number / Page

1 Plot of the formaldehyde-DNPH derivative concentration determined by procedure vs actual concentration 8

2 Plot of the acetaldehyde-DNPH derivative concentration determined by procedure vs actual concentration 9

3 Plot of the acetone-DNPH derivative concentration determined by procedure vs actual concentration. 10

4 Plot of the isobutyraldehyde-DNPH derivative concentration determined by procedure vs actual concentration 11

5 Plot of the methylethylketone-DNPH derivative concentration determined by procedure vs actual concentration 12

6 Plot of the crotonaldehyde-DNPH derivative concentration determined by procedure vs actual concentration 13

7 Plot of the hexanaldehyde-DNPH derivative concentration determined by procedure vs actual concentration 14

8 Plot of benzaldehyde-DNPH derivative concentration determined by procedure vs actual concentration 15

9 Effect of elapsed time on hydrogen cyanide in clear and dark bags. 23

10 The effect of elapsed time on cyanogen in clear and dark bags. 24

11 The effect of elapsed time on hydrogen cyanide in a blend of hydrogen cyanide in clear and dark bags 25

12 The effect of elapsed time on cyanogen in a blend of hydrogen cyanide and cyanogen in clear and dark bags 26

13 The effect of elapsed time on hydrogen cyanide and cyanogen in a dark bag with humid nitrogen 27

14 Total cyanide calibration curve at low concentrations (0-2 ppm) 33

15 Total cyanide calibration curve at low concentrations (0-10 ppm). 34

FIGURES (Cont'd)

Number Page

16 The effect of elapsed time on sample development. 36

17 Time-sample decay curve 38

18 Time-sample decay curve (exhaust only). 48

19 Time-sample decay curve (standard only) 49

20 Time-sample decay curve (exhaust + standard). 50

21 GC peak areas of pentafluorobenzoyl amine derivatives vs time. 59

22 Linearity of monomethylamine GC response (plot on log-log scale). 63

23 Linearity of dimethylamine GC response (plot on log-log scale). 64

24 Linearity of trimethylamine GC response (plot on log-log scale). 65

25 Linearity of monoethylamine GC response (plot on log-log scale). 66

26 Linearity of diethylamine GC response (plot on log-log scale). 67

27 Linearity of triethylamine GC response (plot on log-log scale). 68

28 SO_2 calibration curve 84

29 Detector linearity curve. 91

30 Sample decay curve (short term) 94

31 Sample decay curve (long term). 95

32 Time-Light exposure study (low concentration) 101

33 Time-Light exposure study (high concentration). 102

34 Beer's Law plot for methylene blue. 103

35 Ammonia calibration curve 120

FIGURES (Cont'd)

Number Page

36 Proposed GC flow schematic for analysis of organic sulfides (Step 1). 129

37 Proposed GC flow schematic for analysis of organic sulfides (Step 2). 130

38 Proposed GC flow schematic for analysis of organic sulfides (Step 3). 131

39 Gas chromatograph separation of several organic sulfides in prepared blend. 133

40 Cold trap experiment flow schematic 135

41 Typical gas chromatograph trace of organic sulfides 141

42 Typical GC separation of organic sulfides on acetone-washed Porapak QS column 143

43 Typical organic sulfide separation with Tenax-GC column 144

44 Organic sulfide permeation blend with secondary dilution, near detection limit of GC FPD system 145

45 Organic sulfide permeation blend with secondary dilution, concentrated on Tenax-GC trap and thermally desorbed into GC FPD system 146

46 Carbonyl sulfide linearity plot 151

47 Methyl sulfide linearity plot 152

48 Ethyl sulfide linearity plot. 153

49 Methyl disulfide linearity plot 154

50 Linearity of o-chlorophenol GC response 168

51 Linearity of phenol GC response 169

52 Linearity of salicylaldehyde GC response. 170

53 Linearity of m-cresol and p-cresol GC response. 171

54 Linearity of p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol and 2,4,6-trimethylphenol GC response 172

FIGURES (Cont'd)

Number Page

55 Linearity of 2,3,5-trimethylphenol GC response. 173

56 Linearity of 2,3,5,6-tetramethylphenol GC response. 174

57 Dilution tunnel-CVS system used in qualification experiments. . 179

58 Apparatus for injection of pollutant into dilution tunnel without exhaust 180

59 Apparatus for injection of pollutant into dilution tunnel with exhaust. 181

60 Modified mist generator 182

TABLES

Number Page

1 Physical Properties of the Aldehydes and Ketones (4,5). 4

2 Injection Repeatability 7

3 Multiple Extractions of DNPH Solutions (All units are mg DNPH derivative/mℓ of toluene) 16

4 Percent Recovery of Propionaldehyde 18

5 Experiments Conducted for HCN and C_2N_2 Bag Stability. 22

6 The Effect of Stopper Tip and Absorbing Reagent Concentration on Collection Efficiency at Room Temperature. 29

7 The Effect of Absorbing Reagent Temperature on HCN Collection Efficiency. 31

8 Calibration Curve Linearity at Several Cyanide Concentrations. 32

9 Sample Injection Repeatability for Two Cyanide Concentrations. 35

10 Total Cyanide Gaseous Recovery by Direct CVS Injection. 39

11 Total Cyanide Recovery from Dilute Exhaust Without Filter or With Non-Heated Filter. 39

12 Total Cyanide Recovery from Dilute Exhaust With Heater Filter. 40

13 Important Facts on Individual Hydrocarbons. 45

14 Injection Repeatability on Two Separate Occasions 46

15 List of Individual Organic Amines Included in the Emissions Characterization Inventory. 54

16 Mixing Procedure for Preparation of Pentafluorabenzoylamine Derivatives 58

17 Injection Repeatability Experiments 62

18 Organic Amine Recovery from the CVS Dilution Tunnel Only. . . . 70

TABLES (Cont'd)

Number Page

19 Organic Amine Recovery from the CVS Dilution Tunnel With Exhaust 72

20 Interferences to SO_2 Analysis 79

21 Sulfate Standard Stability. 79

22 SO_2 Collection Efficiency as a Function of Flowrate and Temperature 80

23 Injection Repeatability for Ion Chromatograph 82

24 Calibration Curve for Sulfur Dioxide. 83

25 Sulfur Dioxide Recovery from CVS-Tunnel Injection 86

26 Sulfur Dioxide Recovery from Dilute Exhaust by CVS-Tunnel Injection During Hot FTP Driving Cycle. 87

27 Injection Repeatability Over the Range of Detector Linearity. . 92

28 Nitrous Oxide Qualification Experiments - No Vehicle. 96

29 Nitrous Oxide Qualification Experiment With Vehicle Exhaust . . 96

30 The Effect of Sample Flow Rate and Absorbing Reagent Temperature on the Collection Efficiency. 104

31 The Effect of Individual Exhaust Components on the Development of Methylene Blue 105

32 The Effect of Anions on the Development of Methylene Blue . . . 106

33 The Effect of Sulfur Dioxide Interference on the Development of Methylene Blue 107

34 Hydrogen Sulfide Recovery - No Exhaust Present. 108

35 Effect of Ferric Ion Solution on Hydrogen Sulfide Recovery from Dilute Exhaust 109

36 NH_3 Collection Efficiency as a Function of Flowrate and Temperature 115

37 Injection Repeatability for Ion Chromatograph 117

38 Repeatability of Ammonia Standard 116

TABLES (Cont'd)

Number Page

39 Calibration Curve for Ammonia 119

40 Sample and Standard Stability as a Function of Time 121

41 Ammonia Recovery from CVS-Tunnel, No Exhaust. 122

42 Ammonia Recovery from Dilute Exhaust (No Heated Filter) 124

43 Ammonia Recovery from Dilute Exhaust, Heated Filter 125

44 List of Sulfur Compounds Included in the Analysis of Organic Sulfides. 127

45 List of Chemical and Physical Characteristics of Various Sulfur Compounds Potentially Present in Automotive Exhaust. . 134

46 The Effect of Cold Trapping at -78°C on Carbonyl Sulfide and Methyl Sulfide at Various Concentrations, Flow Rates and Trap Sizes. 136

47 The Effect of Cold Trapping at -196°C on Carbonyl Sulfide and Methyl Sulfide with Various Trap Sizes. 138

48 The Efficiency of Various Materials Trapping Sulfides at Several Temperatures. 139

49 Injection Repeatability for the Organic Sulfides. 148

50 Trap Repeatability for Organic Sulfide Collection 149

51 Trap-to-Trap Repeatability for Organic Sulfide Collection . . . 149

52 Percent Recoveries of the Organic Sulfides from the CVS Tunnel Only 156

53 Percent Recoveries of the Organic Sulfides from the CVS Tunnel and Exhaust. 157

54 Physical Properties of Phenols Possible in Exhaust. 158

55 Extractions with Methylene Chloride 161

56 Extractions with Ether. 162

57 Extraction Efficiency as a Function of pH of Aqueous Solution . 160

58 Effect of Reducing Sample Volume by Kuderna Danish Concentrator on Phenol Recovery. 163

TABLES (Cont'd)

Number Page

59 Effect of Diesel Fuel on Recovery of Phenol 164

60 Interferences to Phenol Recovery or Analysis. 165

61 Linearity Ranges of Internal Standard and of Phenols in Exhaust 167

62 Injection Variability of Phenol 175

63 Baseline Phenol Emission Levels from Mercedes 240D Diesel . . . 175

64 Percent Recoveries from Injection of Phenol into Exhaust of Mercedes 240D Diesel. 176

65 Analytical Procedures of Emissions Characterization 185

SECTION 1

INTRODUCTION

The objective of this project is to evaluate the emissions of regulated and nonregulated pollutants in the exhaust of vehicles having advanced-concept powerplants. Examples of engine types which are being considered for testing in this project include gas turbines, Stirling cycle, turbocharged Diesel, Rankine cycle, stratified charge, and advanced Otto-cycle. The first phase of this project includes the development of analytical technology to provide qualitative and quantitative measurements of unregulated exhaust products of the engines to be tested. This report is a summary of the results of this phase of the project.

Candidate analytical procedures were selected for each of the following compounds or groups of compounds.

aldehydes and ketones

hydrogen cyanide + cyanogen

hydrogen sulfide

organic sulfides + carbonyl sulfide

ammonia

organic amines

nitrous oxide

sulfur dioxide

individual hydrocarbons

phenols

N-nitrosodimethylamine

benzo-α-pyrene

soluble sulfate

The procedures selected represent an assessment of the optimum procedures available at the time of this report and with the approval of the project officer will be used to measure the appropriate unregualted pollutants. Reviews of the literature, procedural development work, validation experiments, and qualification experiments are discussed for ten of these analytical procedures.

These ten analytical procedures are listed in the following paragraphs along with the appropriate section of the report in which they are discussed as well as a brief description of the procedure.

Aldehydes and Ketones (Section 2) - The collection of aldehdyes (formaldehyde, acetaldehyde, isobutyraldehyde and hexanaldelyde) and ketones (acetone and methylethylketone) is accomplished by bubbling CVS diluted exhaust through glass impingers containing 2,4-dinitrophenylhydrazine (DNPH) in dilute hydrochloric acid. The aldehydes and ketones (also knwon as carbonyl compounds) react with the DNPH to form their respective phenylhydrazone derivatives. These derivatives are insoluble or only slightly soluble in the DNPH/HCl solution and are removed by filtration followed by pentane extractions. The filtered precipitate and the pentane extracts are combined and then the pentane is evaporated in the vacuum oven. The remaining dried extract contains the phenylhydrazone derivatives. The extract is dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. A portion of this dissolved extract is injected into a gas chromatograph and analyzed using a flame ionization detector.

Total Cyanide (Hydrogen Cyanide plus Cyanogen) (Section 3) - The collection of total cyanide is accomplished by bubbling CVS diluted exhaust through glass impingers containing a 1.0 N potassium hydroxide absorbing solution. This solution is maintained at ice bath temperature. An aliquot of the absorbing reagent is then treated with KH_2PO_4 and Chloramine-T. A portion of the resulting cyanogen chloride is injected into a gas chromatograph equipped with an electron capture detector (ECD). External CN^- standatds are used to quantify the results.

Individual Hydrocarbons (Section 4) - For measurement of selected individual hydrocarbons, methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2), propane (C_3H_8), propylene (C_3H_6), benzene (C_6H_6), and toluene (C_7H_8), a sample of CVS diluted exhaust is collected in a Tedlar bag. This bagged sample is then analyzed for individual hydrocarbons using a gas chromatographic system containing four separate columns and a flame ionization detector. The peak areas are compared to an external calibration blend and the individual hydrocarbon concentrations are obtained using a Hewlett-Packard 3354 computer system.

Organic Amines (Section 5) - The collection of organic amines (monomethylamine, monoethylamine and dimethylamine, trimethylamine, diethylamine, and triethylamine) is accomplished by bubbling CVS diluted exhaust through glass impingers containing dilute sulfuric acid. The amines are complexed by the acid to form stable sulfate salts which remain in solution. A portion of this solution is then injected into a gas chromatograph equipped with an ascarite loaded pre-column and a nitrogen phosphorus detector (NPD). External amine standards in dilute sulfuric acid are used to quantify the results.

Sulfur Dioxide (Section 6) - The concentration of sulfur dioxide in dilute exhaust is determined as sulfate using a ion chromatograph. Sulfur dioxide is collected and converted to sulfate by bubbling dilute exhaust through two glass impingers containing a 3 percent hydrogen peroxide absorbing solution. The samples are analyzed on the ion chromatograph and compared to standards of known sulfate concentrations.

Nitrous Oxide (Section 7) - For measurement of nitrous oxide, a sample of the CVS diluted exhaust is collected in a Tedlar bag. This bagged sample is then analyzed for nitrous oxide using a gas chromatograph equipped with an electron capture detector. Calibration blends are used to quantify the results. Gas chromatograph peak areas are obtained using a Hewlett-Packard 3354 computer system.

Hydrogen Sulfide (Section 8) - The collection of hydrogen sulfide is accomplished by bubbling CVS diluted exhaust through glass impingers containing a buffered zinc acetate solution which traps the sulfide ion as zinc sulfide. The absorbing solution is then treated with N,N-dimethylparaphenylene diamine sulfate and ferric ammonium sulfate. Cyclization occurs, forming the highly colored heterocyclic compound methylene blue (3,9-bisdimethylaminophenazothionium sulfate). The resulting solution is analyzed with a spectrophotometer at 667 nm in a 1-cm or 4-cm pathlength cell depending upon the concentration.

Ammonia (Section 9) - Ammonia in CVS diluted automotive exhaust is measured in the protonated form, NH_4^+, after collection in dilute H_2SO_4. The acidification is carried out in a glass impinger maintained at ice bath temperature. A sample from the impinger is analyzed for ammonia in an Ion Chromatograph and the concentration in the exhaust is calculated by comparison to an ammonium sulfate standard solution.

Organic Sulfides (Section 10) - The collection of carbonyl sulfide (COS) and the organic sulfides, methyl sulfide (dimethylsulfide, $(CH_3)_2S$), ethyl sulfide (diethylsulfide, $(C_2H_5)_2S$) and methyl disulfide (dimethyldisulfide, $(CH_3)_2S_2$), is accomplished by passing CVS diluted exhaust through Tenax GC traps at -76°C. At this temperature the traps remove the organic sulfides from the dilute exhaust. The organic sulfides are thermally desorbed from the traps into a gas chromatograph sampling system and injected into a gas chromatograph equipped with a flame photometric detector for analysis. External organic sulfide standards generated from permeation tubes are used to quantify the results.

Phenols (Section 11) - The collection of phenols (phenol; salicylaldehyde; m-cresol and p-cresol; p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol and 2,4,6,-trimethylphenol; 2,3,5,-trimethylphenol; and 2,3,5,6,-tetramethylphenol) is accomplished by bubbling CVS diluted exhaust through two Greenburg-Smith impingers containing 200 mℓ of 1 N KOH. The phenols react with the KOH and remain in solution. The contents of each impinger are acidified and extracted with ethyl ether. The samples are partially concentrated, combined and then further concentrated to about 1 mℓ. An internal standard is added and the volume is adjusted to 2 mℓ. The final sample is analyzed by the use of a gas chromatograph and concentrations of individual phenols are determined by comparison to external and internal standards.

These ten analytical procedures underwent a series of validation and qualification experiments. The validation experiments were carried out to determine if the sampling and instrument parameters were appropriate for the quantitative analysis of dilute exhaust. The qualification experiments were carried out to determine if the compounds of interest could be quantitatively recovered from the Constant Volume Sampler (CVS)-dilution tunnel with and without the presence of exhaust in the tunnel.

Validation experiments included checks for sample stability, sample collection efficiency, detector linearity, interferences, extraction efficiency and repeatability, and analysis repeatability.

Sample stability checks were performed using repeated analyses of the same sample at intervals over a specified period of time and comparing the results to the initial analysis. Aldehydes and ketones (after extraction), total cyanide, individual hydrocarbons, organic amines, sulfur dioxide, nitrous oxide, ammonia, and phenols (after extraction) were found to be stable for several days. The organic sulfides and hydrogen sulfide samples were found to be stable for approximately one day.

Sample collection efficiency experiments were performed by passing a known concentrations of sample through a series of impingers or traps and analyzing each impinger or trap individually for the compound of interest. All the procedures discussed in this report have a collection efficiency of 98% or better. Detector linearity experiments were performed by preparing several samples of various known concentrations and plotting resulting peak areas (or heights) versus the concentrations. All instruments demonstrated linearity of response for expected concentration ranges (sample concentrations above the linear range must be diluted to concentrations that fall within the linear range of the instrument). The organic sulfides must be monitored carefully as traps containing over 200 ng of sample fall beyond the linear range of the flame photometric detector. The sample flow rate can be lowered to prevent overloading the collecting Tenax trap.

To determine the interferences for each procedure, known exhaust components were introduced into the sample to determine their effect on the resultant measurements. Interferences were checked and documented for each procedure. Phthalates were found to interfere with the aldehyde and ketone procedure and may cause erroneous results for crotonaldehyde and benzaldehyde. In the hydrogen sulfide procedure, sulfur dioxide decreases the apparent hydrogen sulfide concentration, and its presence or absence must be recorded. Thiophene and ethyl sulfide can not be effectively separated with the normal gas chromatographic operating conditions and therefore, thiophene must be included as a possible source of error in the analysis for ethyl sulfide. The other procedures have interference that can be avoided if care is taken.

To determine extraction efficiency and repeatability for the aldehyde and ketone and the phenol procedures, several samples of known concentrations were prepared and a number of analyses were performed. The extraction efficiency is approximately 100 percent for the aldehyde and ketone procedure, however the overall repeatability varies up to 15 percent at concentrations of 0.2-2.0 mg derivative per mℓ toluene. The results of extraction repeatability experiments for aldehyde and ketone DNPH derivative concentrations below 0.025 mg DNPH derivative per mℓ toluene indicate that the variability in the extraction process can be very significant (i.e., 0.94 percent for benzaldehyde at 0.016 mg/mℓ). This variability needs to be taken into account when evaluating data obtained using this procedure. The extraction efficiency for the phenol procedure is only about 68 percent due to unavoidable problems in the drying down process. This value is repeatable if the extraction procedure is followed closely. These losses must be taken into account when analyzing data obtained from the phenol procedure.

To determine analysis repeatability, several samples of known concentrations were prepared and a number of complete analyses were performed at each concentration. The results of these tests were then compared to determine analyses repeatability. The test-to-test repeatabilities are documented for all procedures in this report. In most cases, repeatability is difficult to obtain at the lower concentrations, while the repeatability at high concentrations is easily obtained.

The qualification experiments were performed to determine if the compounds of interest could travel the length of the dilution tunnel in the presence of dilute exhaust without significant loss by reaction with exhaust or the tunnel itself. The compounds were introduced at the same point at which the exhaust enters the tunnel and were sampled at the normal sampling point (see Section 12).

Qualification experiments were carried out on the aldehyde and ketone, organic amine, sulfur dioxide, nitrous oxide, hydrogen sulfide, total cyanide, organic sulfide, ammonia, and phenol procedures to determine the recovery of known amounts of each pollutant from the CVS tunnel with and without exhaust (phenols CVS dilution tunnel with exhaust only). Aldehydes and ketones, sulfur dioxide, nitrous oxide, total cyanide and phenols can be recovered quantitatively from the CVS dilution tunnel with and without (not done for phenols) exhaust. There is a 10 percent loss of hydrogen sulfide with and without exhaust present. The organic amines, ammonia, and the organic sulfides experience significant losses in the CVS dilution tunnel with and without exhaust present.

Despite the fact that the analytical procedures for the organic amines and the organic sulfides have procedural detection limits of 2 and 0.2 ppb respectively, the losses in the dilution tunnel could prevent the detection of organic amines at levels lower than 20 ppb and the detection of organic sulfides at levels lower than 10 ppb in dilute exhaust. At ammonia levels of 5-10 ppm there is a 25 percent loss of ammonia to the dilution tunnel and an additional fifteen percent loss to exhaust.

The procedures discussed in this report have been found to be the optimum procedures at the time of this report for collecting and analyzing dilute exhaust samples and are recommended for use in this project.

A finalized copy of the analytical procedures discussed in Section 2-11, the BCA sulfate procedure, and DMNA procedure, sampling conditions for DMNA, and an outline for BaP collection and analysis are included as an appendix. The literature search, procedural development work, and validation experiments for some of the compounds were carried out under another EPA Contract, 68-02-2497 (1). The procedures discussed in this report were developed for the measurement of pollutants in dilute exhaust. The use of these procedures for the measurement of pollutants in raw exhaust is not recommended without additional validation and qualification work to document the acceptability of the procedures.

SECTION 2

ALDEHYDE AND KETONE PROCEDURE

LITERATURE SEARCH

The individual aldehydes and ketones that are included in this analysis are: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, isobutyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde. Acetone, acrolein, and propionaldehyde are not resolved from each other under normal gas chromatographic operating conditions and all three are reported together as acetone. The common names, the International Union of Chemists approved names, the chemical formulas, the molecular weights, the melting points, the boiling points, the densities, the molecular weights of the 2,4 dinitrophenylhydrazone derivatives, and the melting points of the 2,4 dinitrophenylhydrazone derivatives are presented in Table 1. The aldehydes and ketones have a characteristicly pungent odor, are flammable, are photochemically reactive, can cause respiratory problems, and are severe eye irritants. The 1976 American Conference of Government Industrial Hygienists has recommended threshold limit values for several of the aldehydes and ketones (2). These values range from 0.1 ppm for acrolein to 1000 ppm for acetone. Other values listed were 2 ppm for formaldehyde and crotonaldehyde, 100 ppm for acetaldehyde and 200 ppm for methylethylketone.

PROCEDURAL DEVELOPEMENT

A procedure, which is already in use at Southwest Research Institute, developed by the Mobile Source Emissions Research Branch of the ESRL-EPA at Research Triangle Park, North Carolina, was selected for the analysis of the aldehydes and ketones (3). This procedure involves bubbling exhaust through glass impingers containing 2,4 dinitrophenylhydrazine (DNPH) in dilute hydrochloric acid. The exhaust sample is collected continuously during a test cycle. The aldehyde and ketones (also known as carbonyl compounds) react with the DNPH to form their respective phenylhydrazone derivatives. These derivatives are either insoluble or only slightly soluble in the DNPH/HCl solution and are removed by filtration followed by pentane extractions. The filtered precipitate and the pentane extracts are combined, and the pentane is evaporated in a vacuum oven. The remaining dried extract contains the phenylhydrazone derivatives. The extract is dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. A portion of this extract is injected in to a gas chromatograph and analyzed using a flame ionization detector. A copy of this procedure as used by the Department of Emissions Research at Southwest Research Institute will be included as an attachment to this report.

TABLE 1. PHYSICAL PROPERTIES OF THE ALDEHYDES AND KETONES (4,5)

Aldehyde or Ketone	ICU Name	Chemical Formula	Molecular Weight	Melting Point	Boiling Point	Density	Molecular Weight DNPH Derivative	Melting Point Der.
Formaldehyde	Methanal	CH_2O	30.03	- 92	- 21	0.815	210.15	167
Acetaldehyde	Ethanal	CH_3CHO	44.05	-121	21	0.783	224.19	168
Acetone	2-Propanone	CH_3COCH_3	58.08	- 95	56	0.790	238.21	128
Propionaldehyde	Propanal	CH_3CH_2CHO	58.08	- 81	49	0.806	238.21	156
Acrolein	Propenal	$CH_2{:}CHCHO$	56.07	- 87	53	0.841	236.20	165
Isobutyraldehyde	2-Methylpropanal	$CH_3CH(CH_3)CHO$	72.11	- 65	63	0.794	252.23	182
Methylethylketone	2-Butanone	$CH_3COCH_2CH_3$	72.11	- 84	80	0.805	252.23	---
Crotonaldehyde	trans2-Butenal	$CH_3CH{:}CHCHO$	70.09	- 74	105	0.850	250.21	190
Hexanaldehyde	Hexanal	$CH_3(CH_2)_4CHO$	100.16	- 56	128	0.814	279.28	104
Benzaldehyde	Benzenecarbonal	C_6H_5CHO	106.13	- 25	178	1.042	286.25	237

VALIDATION EXPERIMENTS

Several experiments were carried out to determine the validity of the DNPH procedure for the analysis of the aldehydes and ketones. These experiments included checks for: GC injection variability, linearity of detector response, sample stability in the DNPH absorbing solution and in toluene, trapping efficiency of the DNPH/HCl solution, interferences, and extraction plus injection repeatability.

The finalized sampling conditions used to collect the aldehydes and ketones are listed below as is a discussion on their selection. Two glass impingers in series, each containing 40 mℓ of 2 N HCl/2,4 dinitrophenylhydrazine, are used to collect the aldehydes and ketones. The two impingers together trap 98+ percent of the carbonyl compounds. This collection efficiency was determined by bubbling known amounts of the aldehydes and ketones through a series of impingers and analyzing each impinger separately. No advantage was found in using more than two impingers. There was no observed difference in analyzing the contents of the two impingers separately or combined. Since the analysis of the two impingers combined is less manpower intensive, the two impingers are analyzed together. During sampling, the two impingers are kept in a 0°C ice bath. The ice bath offers no significant advantage in collection efficiency over room temperature, but does provide a stable sampling temperature during the test. The 0°C temperature also lowers the vapor pressure of the aqueous absorbing solution and thus prevents loss of any significant amount of water from the absorbing solution during sampling. The sample flow rate through the impingers is maintained at 4 liters a minute. This flow provides the largest amounts of sample to flow through the absorbing reagent without loss in absorbing efficiency or the physical loss of any absorbing reagent. A heated filter is used to prevent diesel particulate from contaminating the sampling system. The filter and the line connecting the filter to the dilution tunnel are heated to 375°F to prevent the aldehydes and ketones from being retained on the removed particulate. A Teflon line connecting the filter to impingers is heated to 175°F in order to prevent water from condensing in the sample line. Some of the aldehydes and ketones are water soluble, and the condensation of water in the sample line could cause a significant loss of sample in the sample line.

The HCl/DNPH absorbing reagent has been found to be stable over several days; however, to prevent the possibility of contamination or the inadvertant use of "old" absorbing reagent, the solution is prepared daily as needed.

The samples have been found to be stable for at least two days in the absorbing reagent. However, to prevent the possibility of contamination of the samples by their standing in the lab for prolonged periods, the samples are extracted, dried, and dissolved in toluene all in the same day. Once the sample is dissolved in toluene it is stable for relatively long periods of time. Samples run and re-run over a period of two weeks showed no significant change in concentrations.

To determine the GC injection repeatability for the procedure over a wide range of concentrations, four standards containing 1.6, 0.2, 0.02 and 0.002 mg of each aldehyde and ketone DNPH derivative per mℓ of toluene were prepared. These are the concentration ranges expected when sampling dilute exhaust. Each standard was injected into the GC five consecutive times. The concentration determined by the procedure for each of the derivatives was averaged over the 5 runs, and a standard deviation as well as a percent standard deviation was calculated. The results of these injection repeatability experiments are presented in Table 2. The injection repeatability is good for the 1.6 mg derivative/mℓ toluene standard (percent deviation ranges from 1.1 percent for formaldehyde to 9.6 percent for benzaldehyde) and the 0.2 mg derivative/mℓ toluene standard (percent deviation ranges from 0.5 percent for acetaldehyde to 5.9 percent for benzaldehyde). At the two lower concentrations, the standard deviation in the injection repeatability was found to be much larger. The 0.02 mg derivative/mℓ toluene standard gave percent deviations ranging from 3.7 percent for acetone to 32 percent for benzaldehyde. The 0.002 mg derivative/mℓ toluene standard gave percent deviations which ranged from 10 percent for formaldehyde to 110 percent for benzaldehyde. It appears from the data that the injection repeatability is good at higher derivative concentrations, but much more erratic at very low concentrations.

To determine the linearity of the detector for the concentration ranges of interest for each of the derivatives, seven standard solutions were prepared which contained 8.0, 4.0, 1.6, 0.8, 0.2, 0.02, amd 0.002 mg of each derivative/mℓ toluene. These standards were made by weighing out required amounts of each derivative and dissolving them in the appropriate amount of toluene to give the required concentrations. The solution containing 0.2 mg of each derivative/mℓ toluene was used as the standard and the other six solutions were compared to this standard. Figures 1-8 show plots of the procedure determined concentration vs the actual concentration on a log-log scale. Acetone, methylethylketone, and crotonaldehyde give linear plots throughout the region of interest. Formaldehyde, acetaldehyde, isobutyraldehyde and hexanaldehyde give linear plots except at the lower concentrations (<0.02 mg derivative/mℓ toluene). Benzaldehyde gives a plot which is not linear above 2.0 mg/mℓ toluene. The benzaledhyde-DNPH derivative is not soluble in toluene at concentrations greater than 2.0 mg/mℓ. This fact should be taken into account if high concentrations of benzaldehyde are expected (>5 ppm for a 23 minute sampling period at 4 ℓ/minute).

An experiment was carried out to determine the extraction repeatability for the DNPH procedure at low concentrations of DNPH-aldehyde derivatives. One liter of DNPH absorbing solution containing small amounts of pure formaldehyde, acetaldehyde, acetone, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde DNPH derivatives was prepared. Seven extractions (80 mℓ for each extraction) were carried out over a period of two weeks. The results from the extractions are presented in Table 3. These results were determined in units of mg DNPH derivative/mℓ of toluene. The values for each of the seven extractions, the average, and the standard deviation are listed for each of the aldehydes and ketones. Multiple injections were

TABLE 2. INJECTION REPEATABILITY

DNPH Aldehyde or Ketone Derivative	1.6 mg derivative/ml Standard			0.2 mg derivative/ml Standard			0.020 mg derivative/ml Standard			0.002 mg derivative/ml Standard		
	Avg. for 5 Inject.	Std. Dev.	% Dev.	Avg. for 5 Inject.	Std. Dev.	% Dev.	Avg. for 5 Inject.	Std. Dev.	% Dev.	Avg. for 5 Inject.	Std. Dev.	% Dev.
Formaldehyde	1.567	0.018	1.1	0.188	0.007	3.7	0.022	0.002	9.1	0.007	0.0007	10
Acetaldehyde	1.727	0.022	1.3	0.201	0.001	0.5	0.024	0.002	8.3	-----	------	--
Acetone	1.617	0.018	1.1	0.210	0.002	0.9	0.027	0.001	3.7	0.002	0.0007	35
Isobutyraldehyde	1.561	0.017	1.1	0.208	0.002	1.0	0.020	0.001	5.6	-----	------	--
Methylethylketone	1.575	0.029	1.8	0.206	0.003	1.5	0.024	0.001	4.2	0.003	0.0007	23
Crotonaldehyde	1.781	0.053	3.0	0.206	0.003	1.5	0.015	0.001	6.7	0.002	0.0007	35
Hexanaldehyde	1.682	0.105	6.2	0.204	0.003	1.5	0.015	0.001	6.7	0.001	0.0007	70
Benzaldehyde	1.710	0.165	9.6	0.222	0.013	5.9	0.025	0.008	32	0.001	0.0011	110

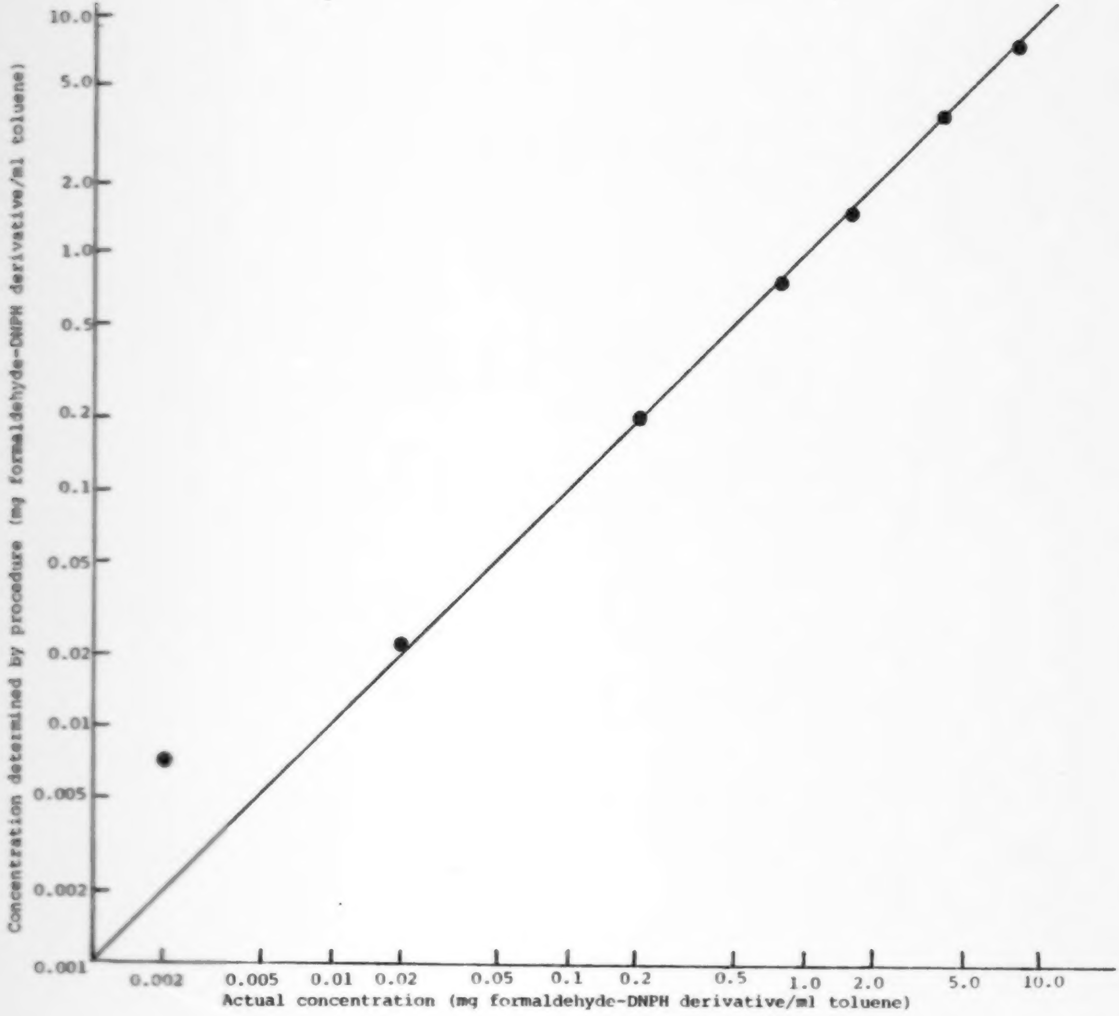


Figure 1. Plot of the formaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

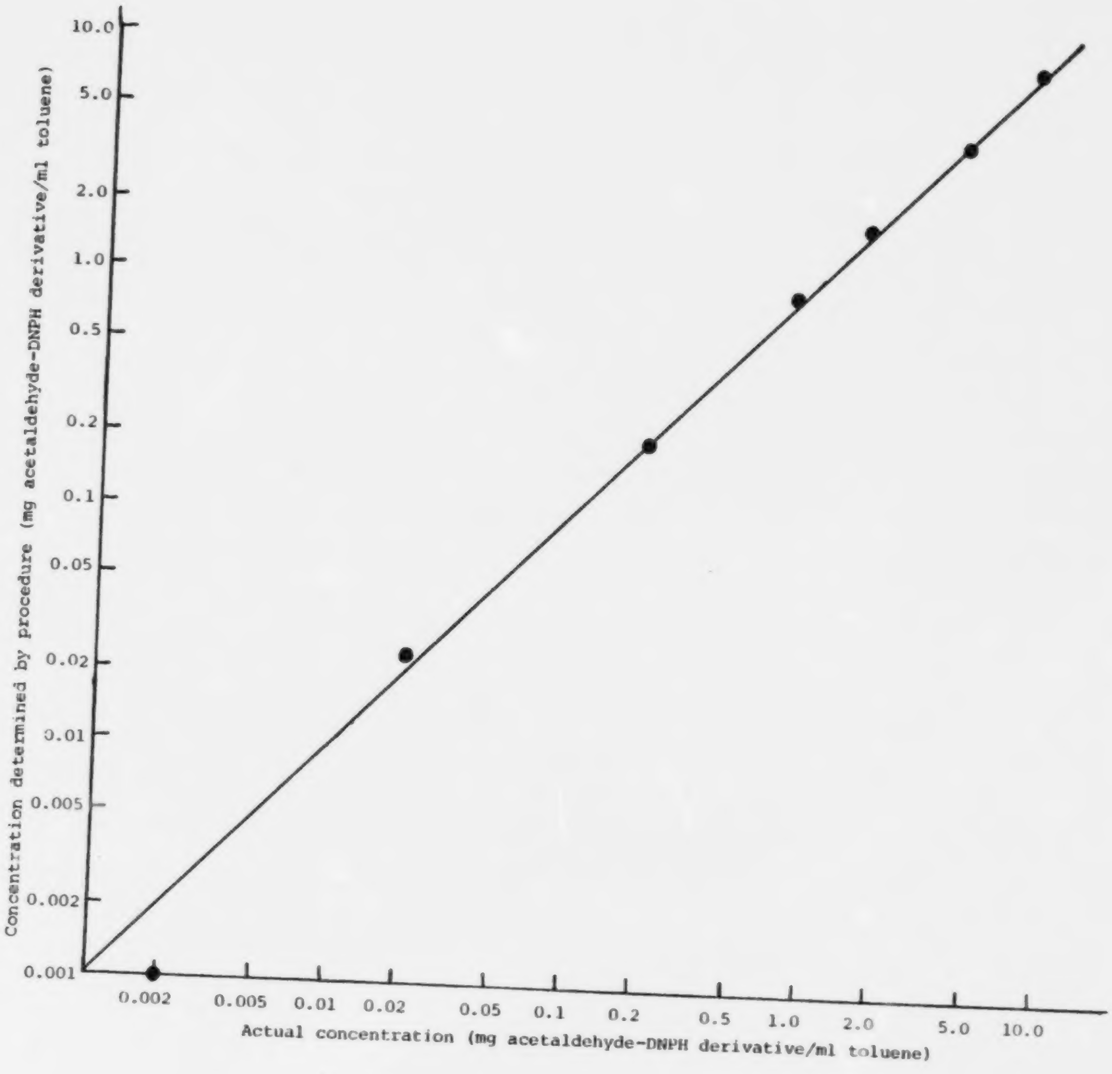


Figure 2. Plot of the acetaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

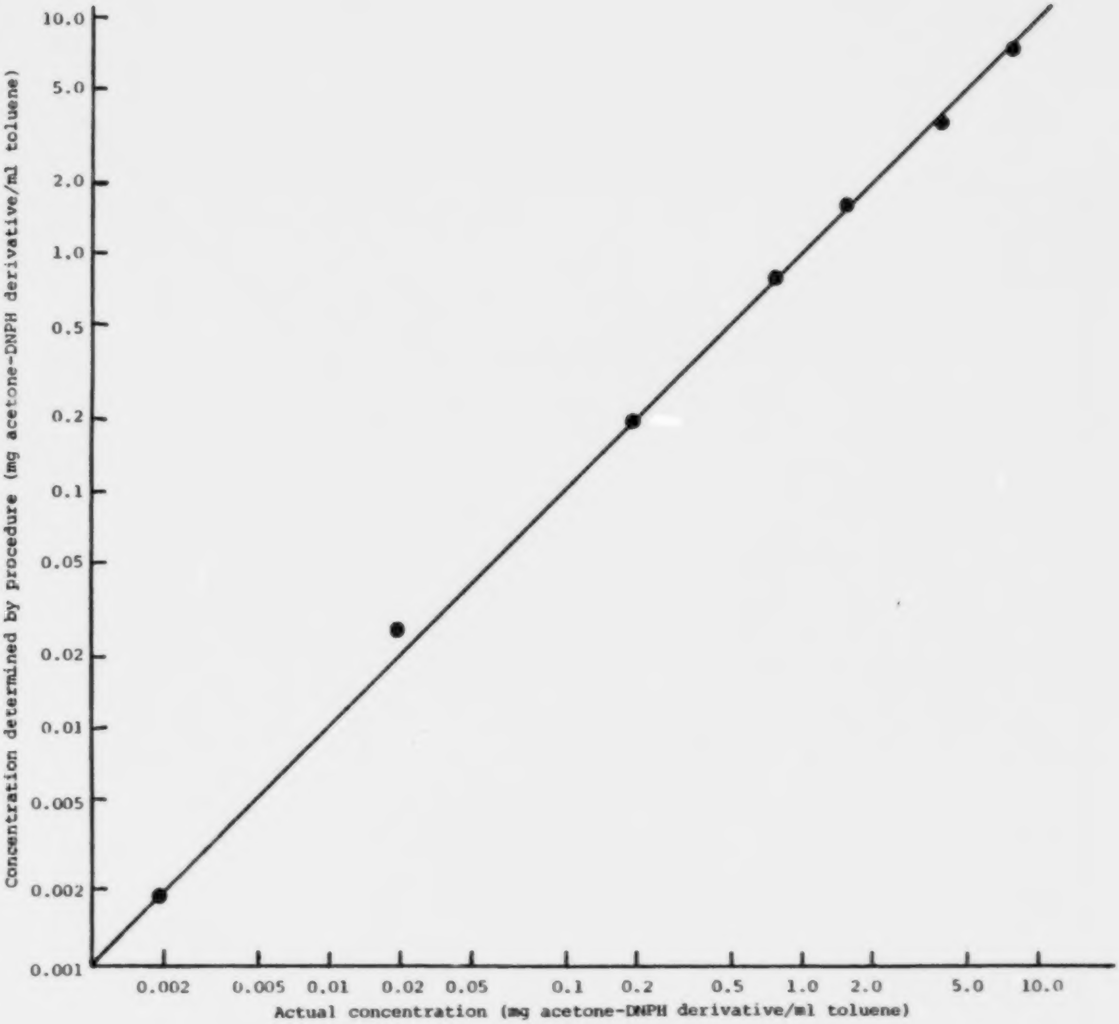


Figure 3. Plot of the acetone-DNPH derivative concentration determined by procedure vs actual concentration.

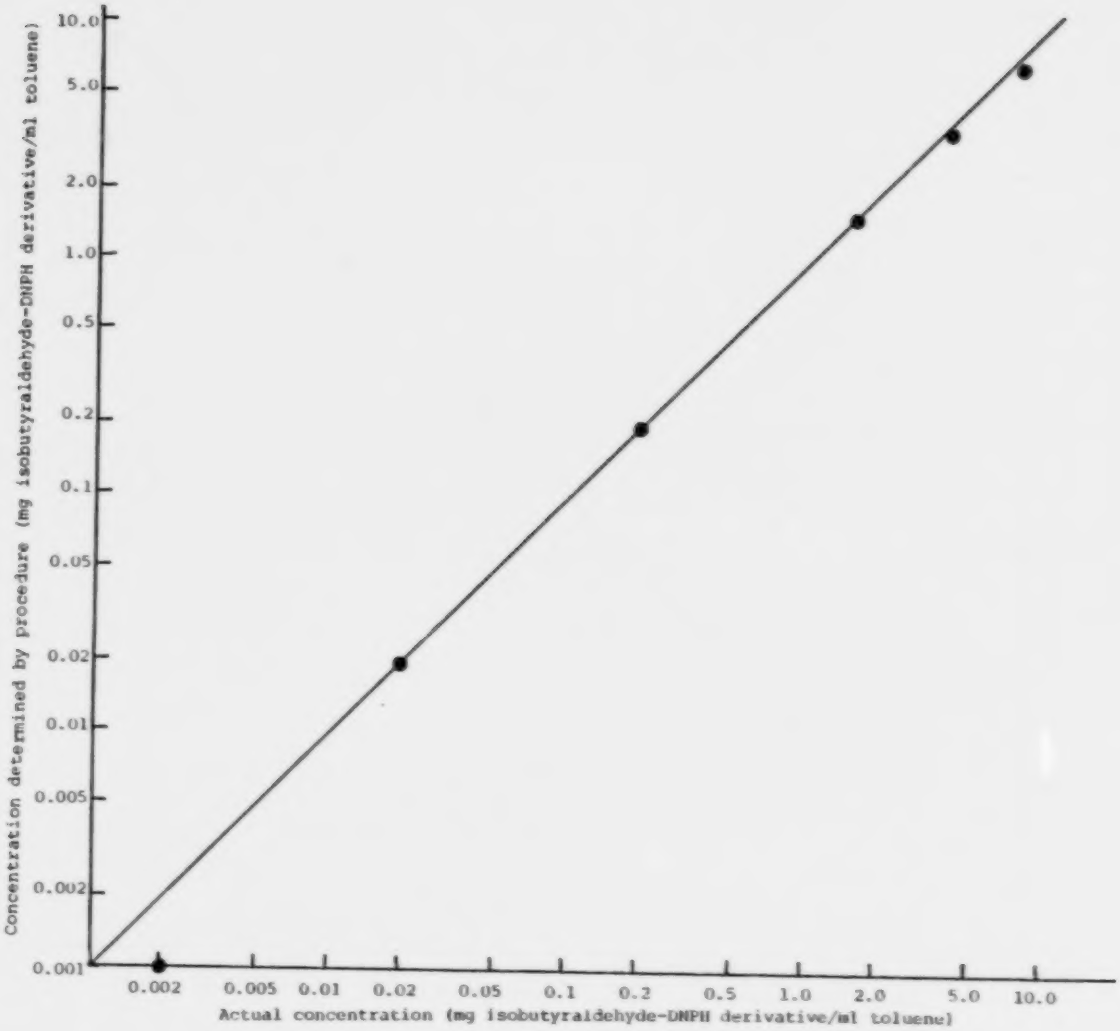


Figure 4. Plot of the isobutyraldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

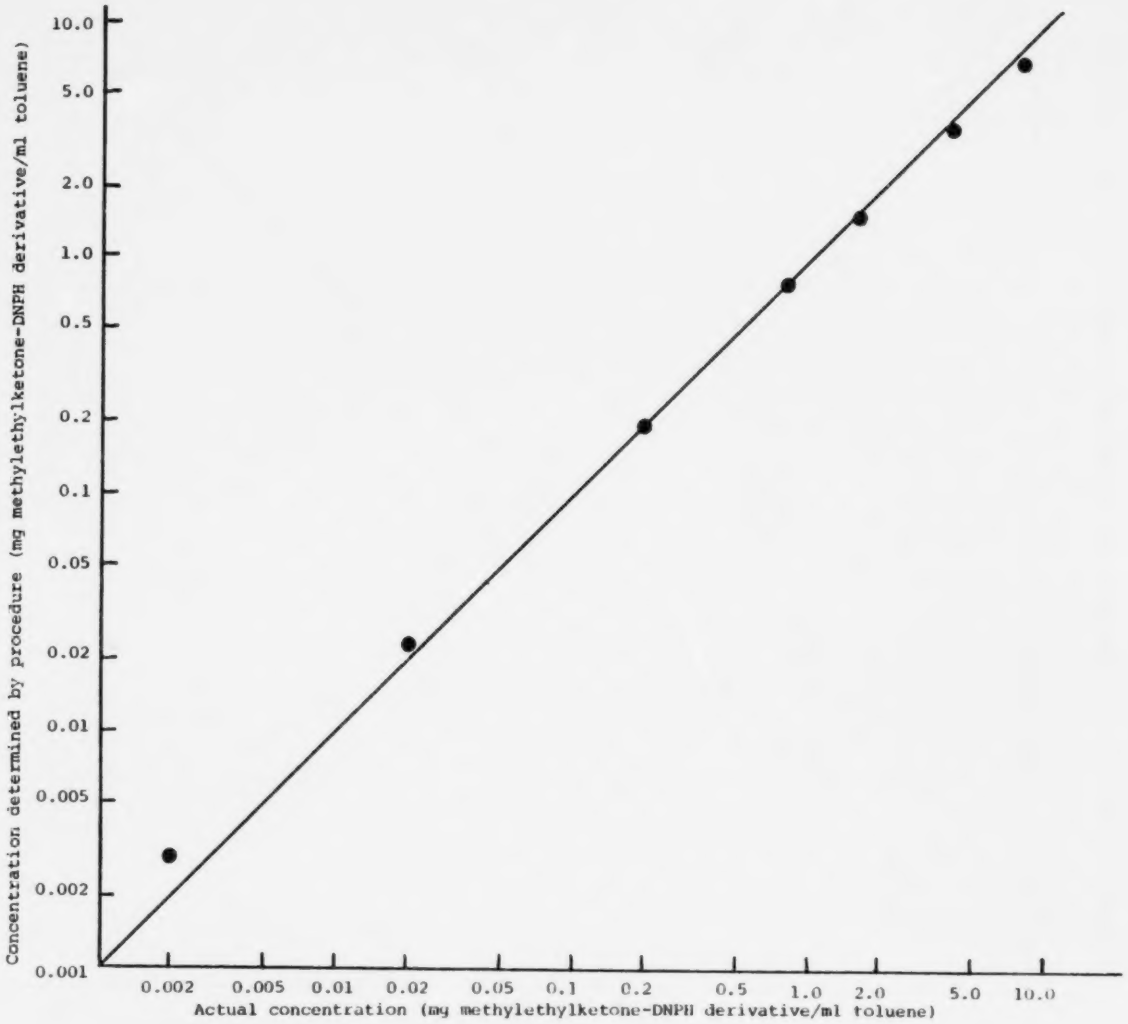


Figure 5. Plot of the methylethylketone-DNPH derivative concentration determined by procedure vs actual concentration.

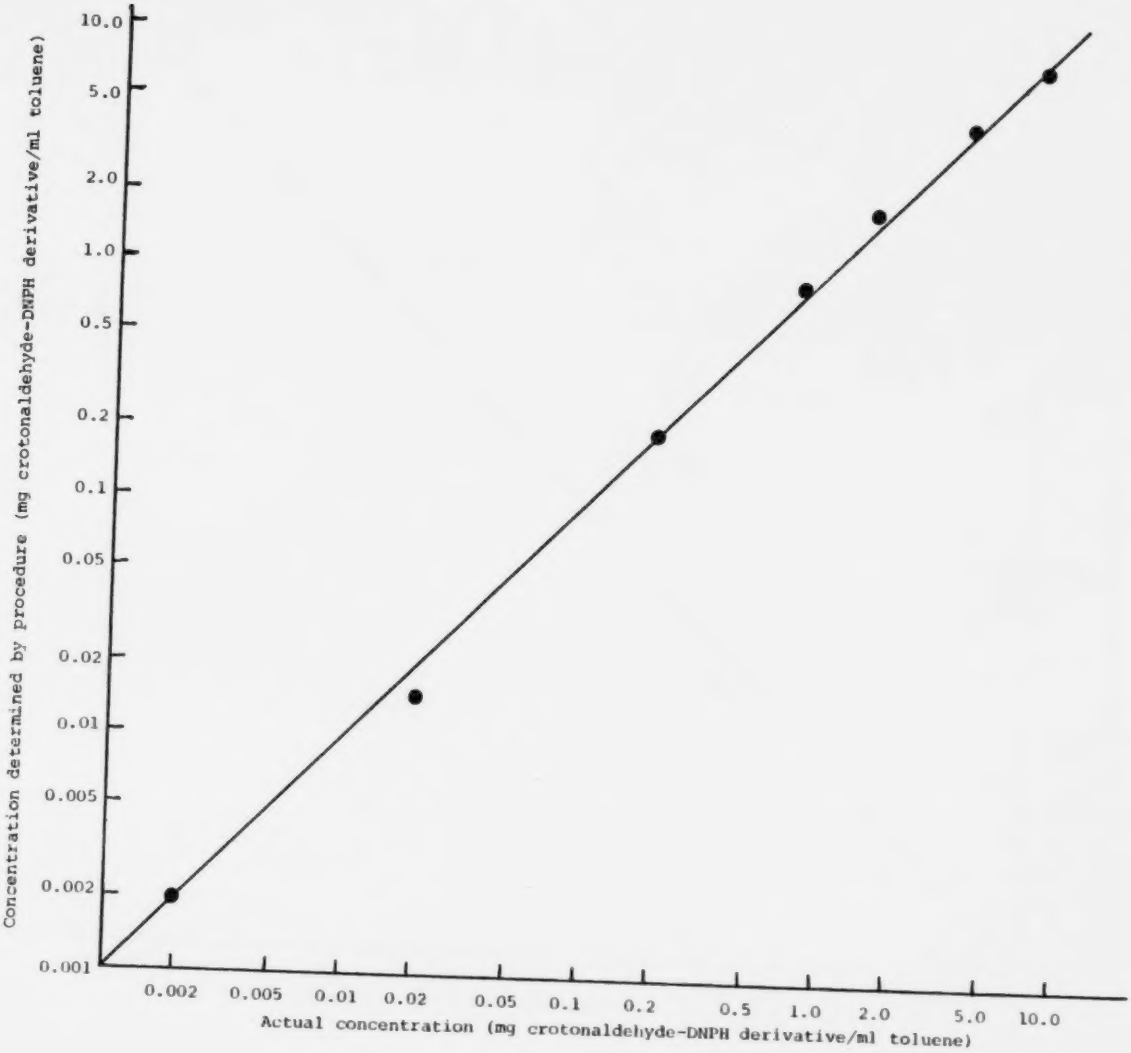


Figure 6. Plot of the crotonaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

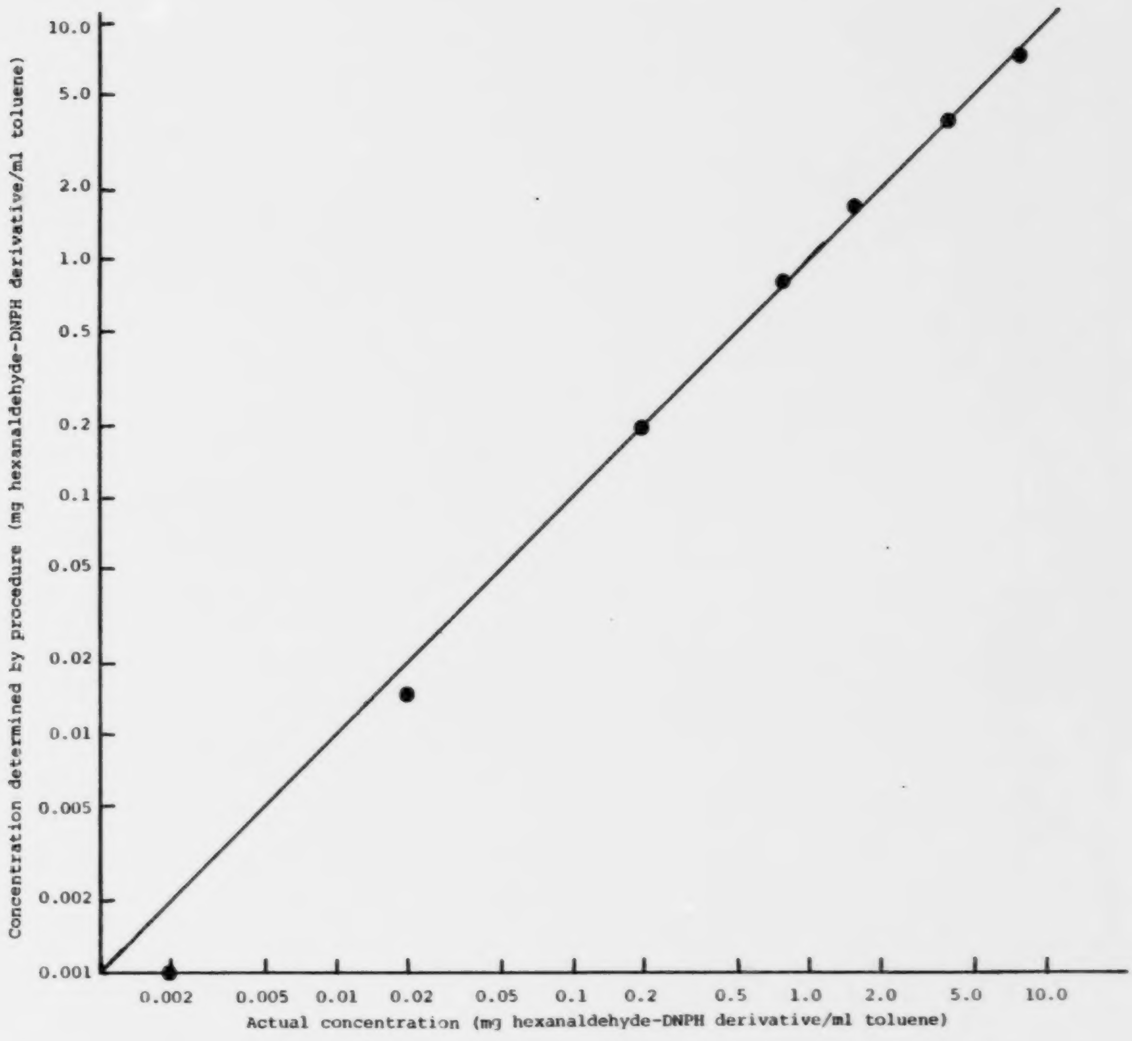


Figure 7. Plot of the hexanaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

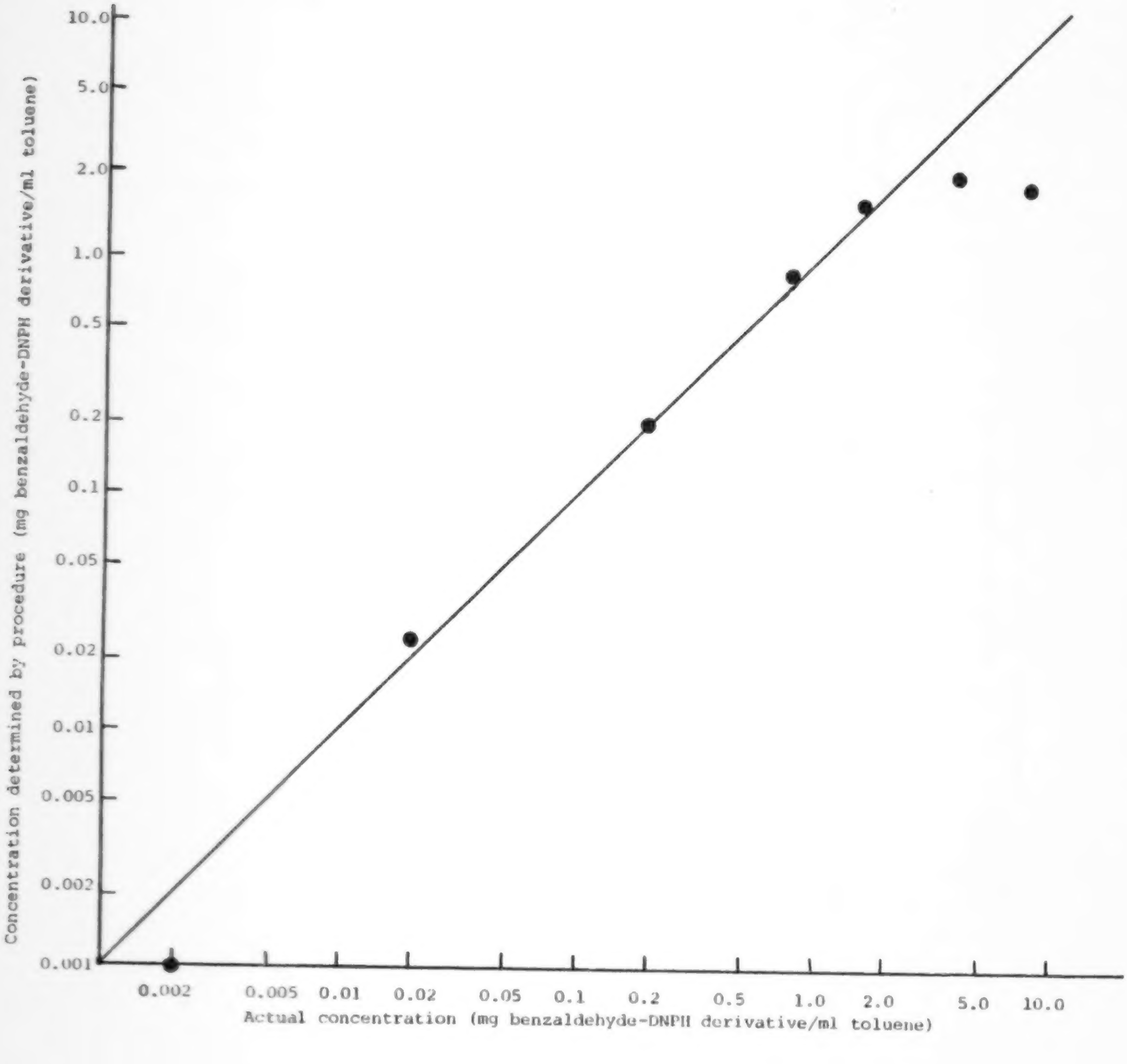


Figure 8. Plot of benzaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

TABLE 3. MULTIPLE EXTRACTIONS OF DNPH SOLUTIONS
(All units are mg DNPH derivative/mℓ of toluene)

Extraction	Form-aldehyde	Acet-aldehyde	Acetone	MEK	Cronton-aldehyde	Hexan-aldehyde	Benz-aldehyde
First	0.018	0.011	0.005	0.000	0.003	0.001	0.014
Second	0.023	0.037	0.015	0.003	0.004	0.002	0.027
Third	0.020	0.032	0.015	0.000	0.003	0.001	0.044
Fourth	0.009	0.013	0.005	0.000	0.002	0.000	0.000
Fifth	0.014	0.019	0.007	0.000	0.003	0.002	0.014
Sixth	0.020	0.031	0.014	0.004	0.005	0.002	0.004
Seventh	0.014	0.027	0.043	0.014	0.004	0.000	0.007
Average	0.017	0.024	0.015	0.003	0.003	0.001	0.016
Standard Deviation	±0.005	±0.010	±0.013	±0.005	±0.001	±0.001	±0.015

also carried out on each sample over the two week period. The values obtained generally did not vary more than 0.002 mg derivative/mℓ toluene (except for two acetone DNPH values). This finding indicates, for several of the compounds, that a large part of the variation in values was due to the extraction process and not the lack of injection repeatability.

The results of these experiments indicate that the variability in the extraction process for concentrations of aldehyde DNPH and ketone DNPH derivatives below 0.025 mg DNPH derivative/mℓ toluene can be very significant (i.e., 94 percent for benzaldehyde at 0.016 mg/mℓ). This variability needs to be taken into account when evaluating data obtained using this procedure. At higher DNPH derivative concentrations (0.2-2.0 mg derivative per mℓ toluene) the overall test variability (trapping, extraction and injection) is approximately 15 percent. This value was obtained from the standard deviation of tunnel recovery and trapping efficiency experiments.

The DNPH analysis for the aldehydes and ketones has given abnormally high concentrations of crotonaldehyde and benzaldehyde in isolated occassions. A gas chromatography-mass spectroscopy study was carried out on three samples obtained from a gasoline powered vehicle. The three samples either contained abnormally high concentrations of crotonaldehyde-DNPH derivative or benzaldehyde-DNPH derivative or both. The results from this study revealed that neither crotonaldehyde nor benzaldehyde was present in the samples. Further gas chormatography-mass spectroscopy studies were carried out on two of the samples to determine what compounds were present. In both samples, the crotonaldehyde peaks were due to a phthalate, and the benzaldehyde peaks could not be identified. This study revealed that the samples contained several other phthalates as well as di-2-ethylhexyladipate (a fuel stabilizer). Many phthalate esters (e.g., dioctyl, dibutyl, dimethyl, etc.,) are found in lubricants and plastics. It is possible that the phthalate peaks found in the above samples were due to contamination in the extraction process (e.g., from a pipette bulb, etc.). In subsequent testing, extreme care will be taken to assure the samples do not come into contact with plastics and other materials which could cause contamination. It is also possible that some of the phthalates which are found in small quantities in the samples are from the exhaust (orignating from lubricants) and are possible interferences in the procedure. Also, the di-2-ethylhexyladipate appears to produce a minor interference.

QUALIFICATION EXPERIMENTS

Qualification experiments were carried out using a Mercedes 240D vehicle. Hot FTP (23 minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel plus vehicle experiments. Aluminum cylinders containing 1350 and 436 ppm propionaldehyde in balance nitrogen were used as the source for aldehydes in the experiments. The cylinders were named using the aldehyde-DNPH procedure. The flow of propionaldehyde into the tunnel was regulated to give concentrations of 0.5-2 ppm propionaldehyde in the dilution tunnel. Injections of propionaldehyde into the tunnel without exhaust gave recoveries that ranged from 85 to 115 percent with an average of 102 percent (Table 4). The recovery of propionaldehyde in the presence of vehicle exhaust and without a heated filter ranged from 59 percent to 89 percent with an average of 76 percent (Table 4). The recovery of propionaldehyde from the dilution tunnel in the presence of exhaust while using a heated filter ranged from 82 to 120 percent for an average of 99 percent (Table 4). The injections with the vehicle were corrected for the vehicle baseline emission of propionaldehyde. If a heated line and filter is used to remove particulate and if propionaldehyde is representative of the aldehydes, then it appears that there is little or no loss of aldehyde in the dilution tunnel with or without vehicle exhaust.

TABLE 4. PERCENT RECOVERY OF PROPIONALDEHYDE

Tunnel Only		Tunnel + Vehicle No Heated Filter		Tunnel + Vehicle Heated Filter	
Run	Recovery %	Run	Recovery	Run	Recovery
1	85	1	83	1	86
2	115	2	86	2	82
3	99	3	89	3	120
4	96	4	76	4	106
5	110	5	64	5	85
6	106	6	59	6	107
Avg	102 ± 11	Avg	76 ± 12	7	103
				8	103
				Avg	99 ± 13

RESULTS AND CONCLUSIONS

The concentration of aldehydes and ketones in dilute exhaust can be determined by (1) trapping the aldehydes and ketones in a DNPH/HCl absorbing solution, (2) removing the resulting derivative from the absorbing solution by filtration and extraction with pentane, (3) evaporating off the pentane (4) dissolving the dried extract in toluene, and (5) analyzing the resulting solution with a gas chromatograph equipped with a flame ionization detector. The aldehydes and ketones are effectively trapped in the absorbing solution at a flow rate of 4 ℓ/minute. The procedure has a minimum detection limit of approximately 5 ppb. This carbonyl concentration in the exhaust gives a corrsponding concentration of 0.002 mg/mℓ in toluene.

The accuracy of the procedure in the 0.5-20 ppm concentration range for the aldehydes and ketones in dilute exhaust is approximately 10-15 percent. The accuracy of the procedure in the 0-0.05 ppm range is not as good and values can vary as much as 100 percent. The gas chromatograph system gives a linear response for acetone, methylethylketone, and crotonaldehyde DNPH derivative concentrations between 0.002 and 8 mg derivative/mℓ toluene and gives a linear response for formaldehyde, acetaldehyde, isobutyraldehyde and hexanaldehyde DNPH derivative concentrations between 0.02 and 8 mg derivative/mℓ toluene. The benzaldehyde-DNPH derivative gives a linear response in the 0.02 to 2 mg derivative/mℓ toluene concentration range. The benzaldehyde derivative is not soluble at concentrations greater than 2 mg/mℓ toluene.

Phthalates and di-2-ethyhexyladipate were found by mass spectroscopy to be interferences in the procedure. Many phthalate esters (e.g., dioctyl, dibutyl, dimethyl, etc.) are found in lubricants and plastics, and di-2-ethylhexyladipate is used as a fuel stabilizer. Contamination from phthalates could occur in the extraction process or in sample storage if the sample is allowed to come into contact with plastics, a pipette bulb, a lubricant, etc. It is also possible that some phthalates originate from the exhaust (from lubricants) and are possible interferences in the procedure. The benzaldehyde and crotonaldehyde values can be affected by these interferences. The interfering peak in the region of benzaldehyde is usually broad and the benzaldehyde peak, if present, can be observed on top of this interference. If care is taken, a reliable value can be determined for the benzaldehyde. Any value reported for crotonaldehyde may be artifically high due to possible phthalate contamination. Extreme care must be taken when handling the sample in order to eliminate any possibility of contamination after collecting the sample and before analysis.

Propionaldehyde can be recovered quantitatively from the dilution tunnel with or without diesel exhaust present if a heated filter is used. If propionaldehyde is representative of the aldehydes and ketones, there is little or no loss of the aldehydes in the dilution tunnel with or without exhaust present.

Overall the DNPH procedure should provide a relatively accurate method for determining the concentration of aldehydes and ketones in dilute exhaust, and its use is recommended for this project.

SECTION 3

TOTAL CYANIDE PROCEDURE

LITERATURE SEARCH

Hydrogen cyanide is a flammable, toxic, and colorless liquid at room temperature and has the characteristic odor of bitter almonds. Some synonyms for hydrogen cyanide are hydrocyanic acid, prussic acid, and formonitrile. Hydrogen cyanide is a covalent molecule and dissociates in an aqueous solution as do the hydrogen halides. Hydrogen cyanide (HCN) has a molecular weight of 27.03, a boiling point of 24.70°C, and a melting point of -13.42°C. It is a linear molecule with C-H and C≡N bond distances of 1.06 and 1.15 Å, respectively. It is a weak monoprotic acid with a dissociation constant of 2.1×10^{-9}. This highly poisonous compound is a respiratory inhibitor and irreversibly combines with the iron complex in the blood, stopping the oxidation processes in tissue cells and causing death by asphyxiation. Commercially, hydrogen cyanide is prepared by reacting methane, ammonia, and air over a platinum catalyst at 1000-1200°C, by the reaction of nitric oxide and gasoline at 1400°C, the reaction of hydrocarbons, ammonia and oxygen at 600-1500°C, and many other methods. Reactions similar to these may be responsible for the hydrogen cyanide produced in exhaust.

Cyanogen is a flammable, toxic, and colorless gas at room temperature and like hydrogen cyanide, has the characteristic odor of bitter almonds. Some synonyms for cyanogen are dicyan, oxalic acid, dinitrile, and oxalonitrile. Pure cyanogen is stable, although the impure gas may polymerize to paracyanogen between 300° and 500°C or by exposure to ultraviolet light. Cyanogen dissociates into CN radicals and can oxidatively add to lower valent metal atoms, giving dicyano complexes. It resembles halogens in the disproportionation reaction in basic solution:

$$(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O$$

Cyanogen (C_2N_2) has a molecular weight of 52.04, a freezing point of -27.9°C and a boiling point of -21.17°C. Cyanogen is a symmetrical and linear molecule with a C-C bond distance of 1.37 Å and a C≡N bond distance of 1.13 Å. Its physiological effect on living tissue is similar to that of hydrogen cyanide. Cyanogen is prepared by many methods: air oxidation of hydrogen cyanide over a silver catalyst at 300-600°C, passage of hydrogen cyanide over cuprous oxide at ambient temperatures, reaction of hydrogen cyanide and chlorine over a surface-active material such as activated charcoal at >700°C, any many others. In all cases above, cyanogen is produced from hydrogen cyanide. Although none of these are exactly applicable for an automotive system, a similar process may be responsible for any cyanogen that is produced.

The analyses for hydrogen cyanide, cyanogen, and/or cyanide ion has been performed by several basic analytical techniques: titration, colorimetry, specific ion electrode, and gas chromatography. The Liebig determination of cyanide ion by titration with silver ion was discarded as a means of analysis because of the low concentrations that were expected from exhaust samples. Colorimetry has previously been used by SwRI and has been found to be manpower intensive. An alternative procedure was sought with this factor in mind. The best means of analysis was with either a specific ion electrode or a gas chromatograph.

Three acceptable procedures were selected from the literature. Sekerka and Lechner (6) reported the use of a cyanide ion-selective electrode for the analysis of cyanide ion in waste water. The specific ion electrode was used in conjunction with a colorimetric technique to determine the reliability of the procedure. The samples were collected in sodium or potassium hydroxide and analyzed potentiometrically. The minimum detectable limit reported was about 2 ppb. The second technique required the use of Tedlar bag samples and subsequent analysis with a gas chromatograph using a nitrogen phosphorus detector (NPD). The third technique reported by Valentour et al (7) was used with biological samples (blood, urine, and gastric contents). The samples were collected in sodium of potassium hydroxide and the trapped cyanide ion was reacted with chloramine-T to produce cyanogen chloride. The cyanogen chloride was then analyzed with a gas chromatograph using an electron capture detector (ECD). After preliminary experiments, the final analytical procedure selected was a significant modification of the Valentour et al procedure.

PROCEDURAL DEVELOPMENT

Attempts to analyze hydrogen cyanide and cyanogen separately were unsuccessful and the details are reported below. The inability to analyze hydrogen cyanide and cyanogen separately led to consideration of several specific procedures for the analysis of hydrogen cyanide and cyanogen in the form of cyanide ion.

Initially, it was decided to determine the concentration of hydrogen cyanide and cyanogen by collecting a bag sample of the dilute exhaust and analyzing it with a gas chromatograph using a nitrogen phosphorous detector. This detector was selected because of its specificity to carbon-nitrogen compounds. Hydrogen cyanide and cyanogen can be resolved with a 6' X 1/4" O.D. glass column packed with 100/120 mesh Porapak QS. Isothermal column temperature operation at 50°C and a helium carrier gas flow rate of 60 mℓ/min were the column conditions. A glass lined injector and interface were also used to preserve sample integrity.

Bag stability experiments with hydrogen cyanide and cyanogen were conducted to determine if sample integrity could be maintained over a short period of time. Bag stability is necessary due to time required to collect the sample and the subsequent waiting period before the sample can be analyzed. The bag sample lifetime should be at least two hours after a sample is collected. Clear and aluminum foil tape covered Tedlar plastic bags were used to conduct bag stability experiments. Dark bags (aluminum foil tape covered) were tested to determine the effect of photochemical decomposition on hydrogen cyanide and cyanogen.

A list of bag stability experiments which were conducted is shown in Table 5. Each bag contained approximately one cubic foot of the dilute gas.

TABLE 5. EXPERIMENTS CONDUCTED FOR HCN AND C_2N_2 BAG STABILITY

Compound	Clear Bags			Dark Bags		
	Nitrogen	Air	Exhaust	Nitrogen	Air	Exhaust
HCN	X	X	X	X	X	X
C_2N_2	X	X	X	X	X	X
HCN & C_2N_2		X	X	X	X	X
HCN & C_2N_2*				X		

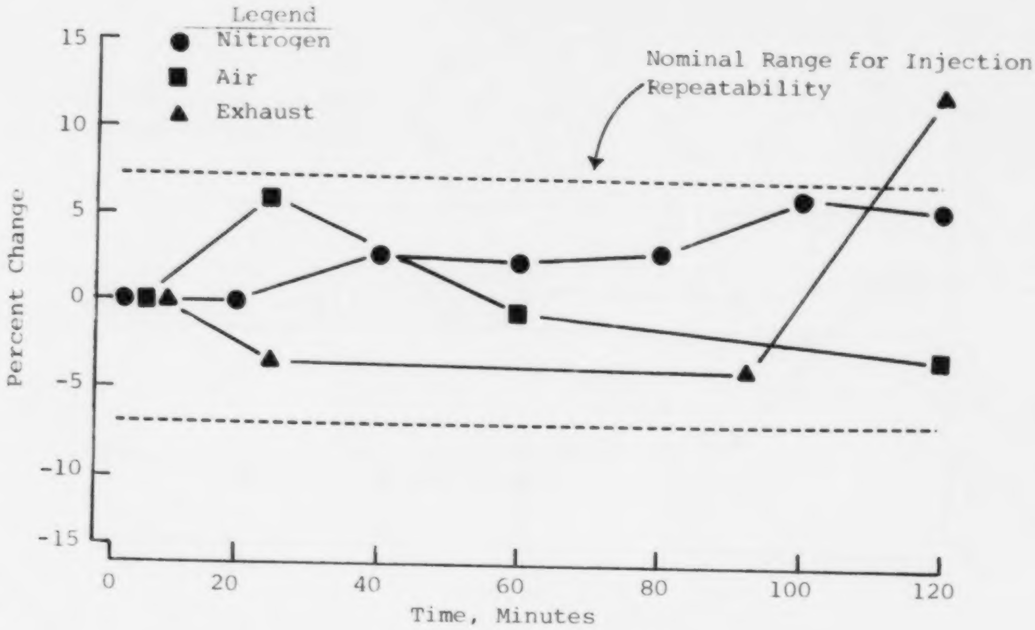
---

* Blend of hydrogen cyanide and cyanogen in humid nitrogen.

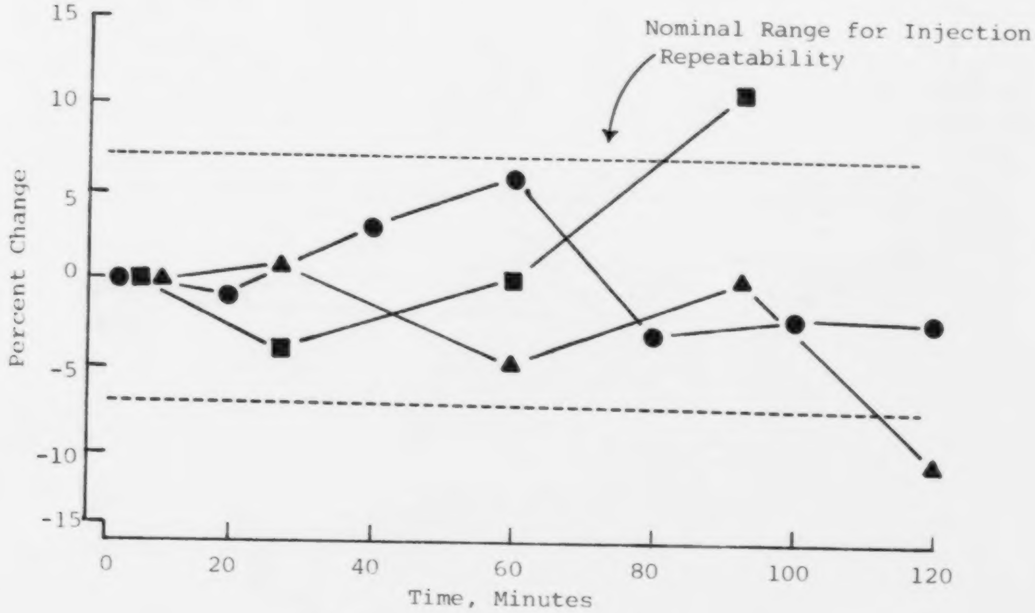
Experiments were conducted with nitrogen, air, dilute exhaust and humid nitrogen. Dilute exhaust was selected at random from bag samples generated during other tests, and humid nitrogen was generated by passing nitrogen through an impinger containing deionized water. Hydrogen cyanide and/or cyanogen were then added to each bag to give a nominal concentration of about 2 ppm. At twenty to thirty minute intervals, 5 mℓ of the gas was removed with a glass gas-tight syringe and injected into the gas chromatograph. The percent change in the concentration was then calculated using the initial injection. Figures 9 through 13 show the effect of elapsed time on the stability of hydrogen cyanide and cyanogen. Figure 9 demonstrates the stability of hydrogen cyanide in clear and dark bags with a variety of atmospheres. Peak areas for hydrogen cyanide remained within the nominal range of injection variability for at least 80 minutes, and no definite trends were observed. (The nominal range of injection variability was set at ± 7 percent and is indicated in all figures by a dotted line). On the other hand, cyanogen showed a considerable percent loss in the clear bags with both nitrogen and exhaust (Figure 10). In the dark bag, cyanogen remained stable except in the presence of exhaust.

Figures 11 and 12 show the effect of a blend of hydrogen cyanide and cyanogen in clear and dark bags with the various atmospheres. Again, hydrogen cyanide was stable within the limits of injection variability for a short period of time. In both cases, hydrogen cyanide was stable on the order of about 60 minutes. Cyanogen behaved similarly to hydrogen cyanide in the clear bag, but a steady decrease in concentration was observed in all atmospheres with the dark bag.

In humid nitrogen (Figure 13) there was a 70 percent loss of hydrogen cyanide after only 20 minutes. After this initial loss, the level of hydrogen cyanide remained relatively constant. Cyanogen under the same conditions

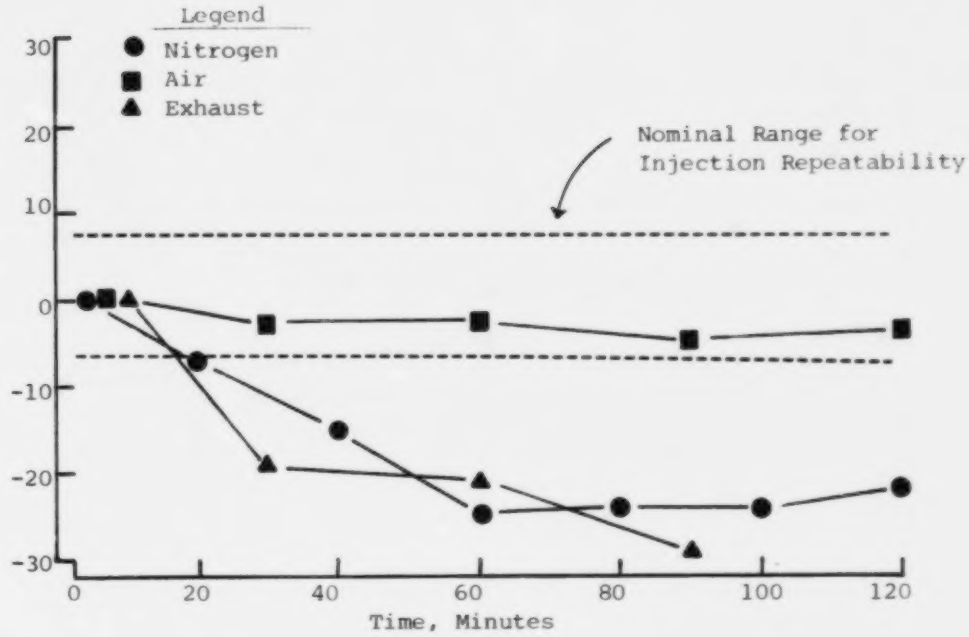


Hydrogen cyanide in clear bags

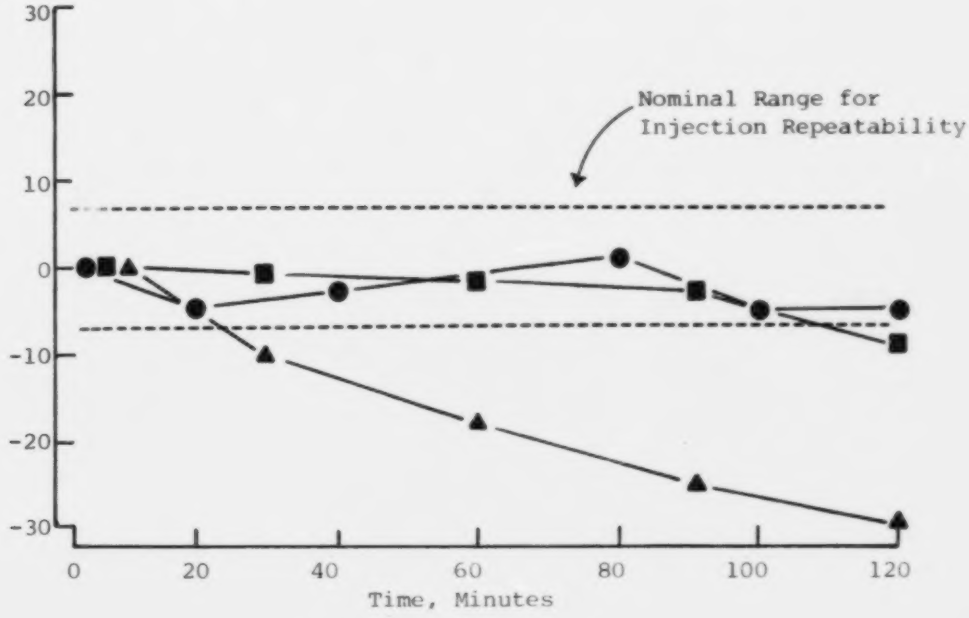


Hydrogen cyanide in dark bags

Figure 9. Effect of elapsed time on hydrogen cyanide in clear and dark bags.

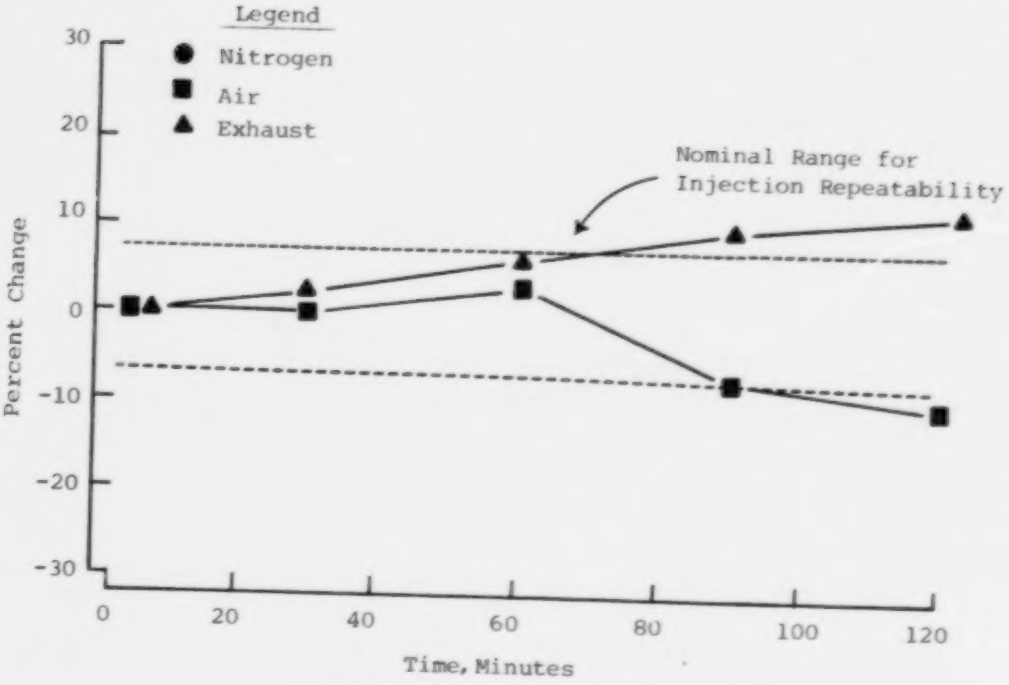


Cyanogen in clear bags

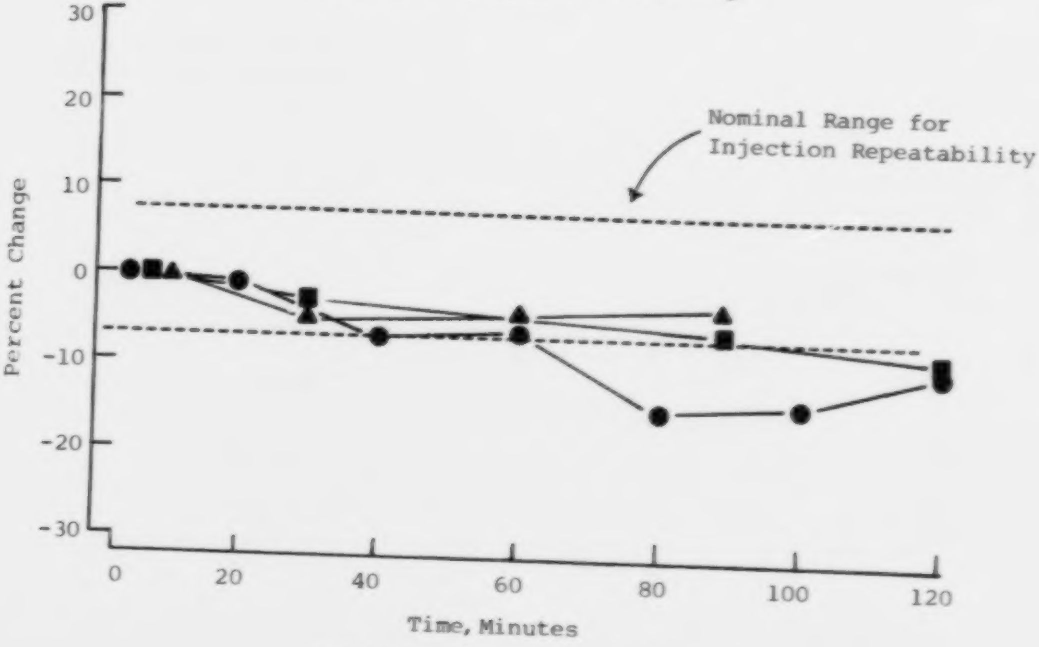


Cyanogen in dark bags

Figure 10. The effect of elapsed time on cyanogen in clear and dark bags.

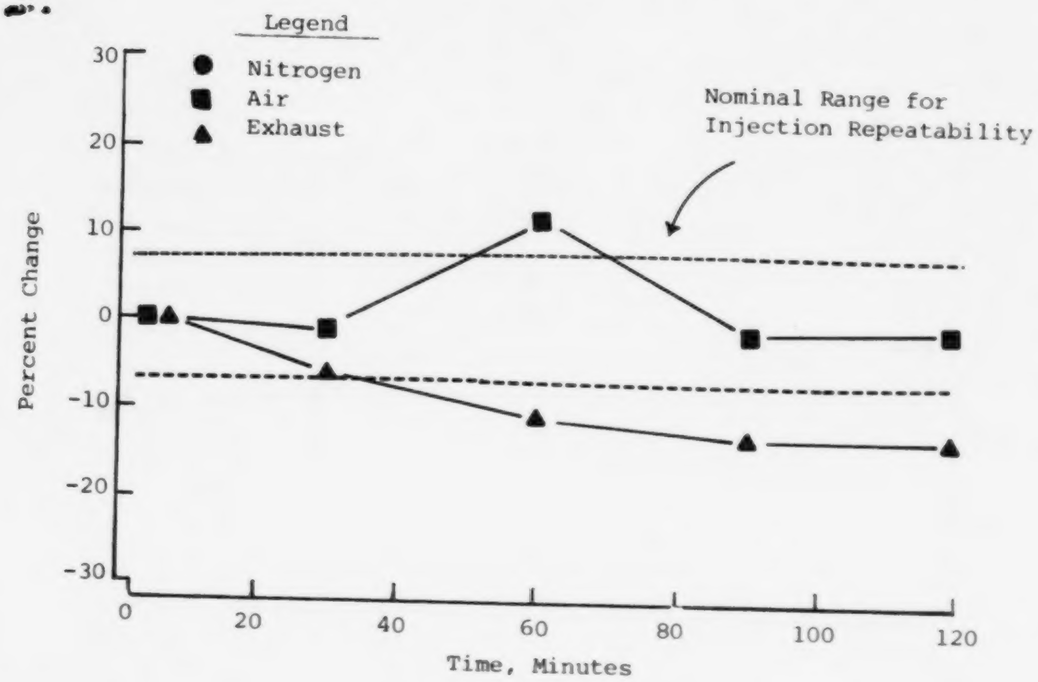


Hydrogen cyanide in clear bags

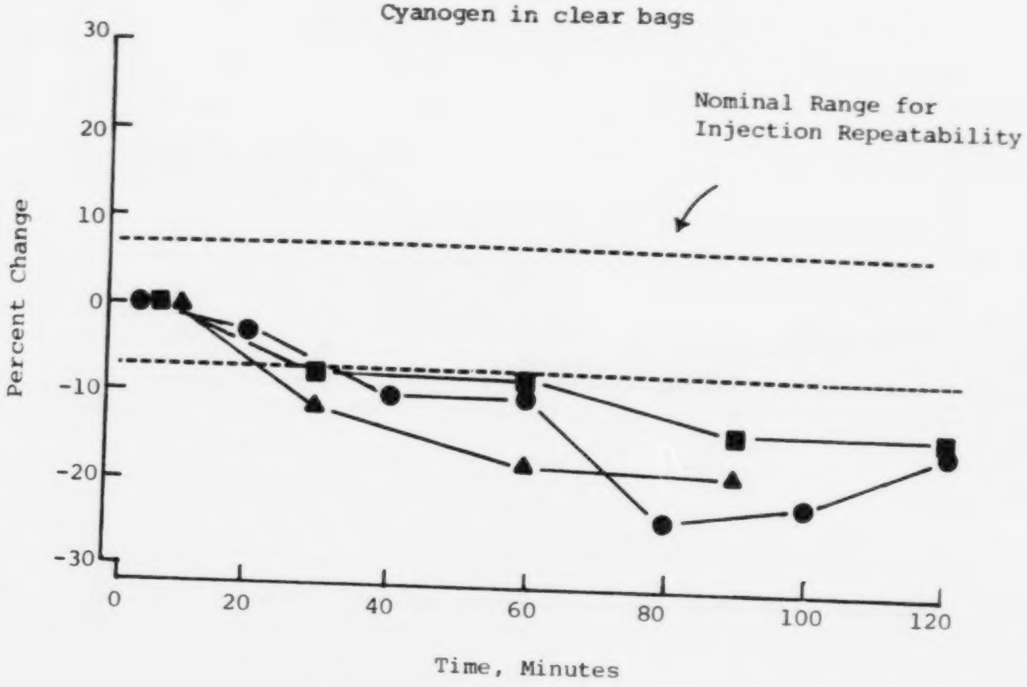


Hydrogen cyanide in dark bags

Figure 11. The effect of elapsed time on hydrogen cyanide in a blend of hydrogen cyanide and cyanogen in clear and drak bags.



Cyanogen in clear bags



Cyanogen in dark bags

Figure 12. The effect of elapsed time on cyanogen in a blend of hydrogen cyanide and cyanogen in clear and dark bags.

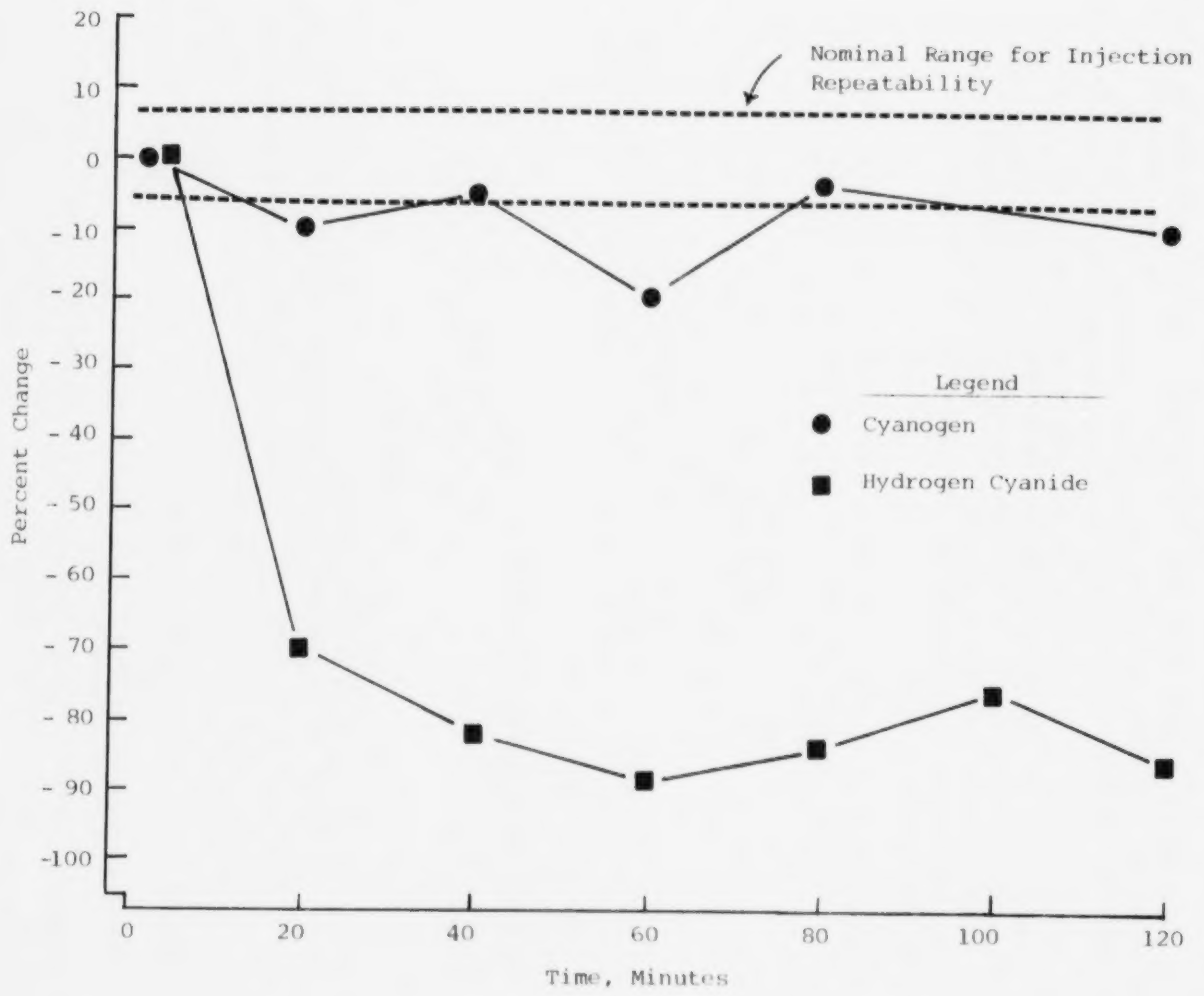


Figure 13. The effect of elapsed time on hydrogen cyanide and cyanogen in a dark bag with humid nitrogen.

showed only a slight decrease in concentration.

The short bag lifetime of hydrogen cyanide and cyanogen prevent the use of grab samples of exhaust. At this point, the alternative procedures were investigated for the analysis of hydrogen cyanide and cyanogen. These techniques required samples to be collected in an aqueous solution.

At the same time the work with bag samples was underway, efforts to develop a procedure using the specific ion electrode were being conducted. Potassium cyanide standard solutions were prepared with 0.1 M potassium hydroxide. A calibration curve was to be determined by plotting the measured potential in millivolts as a function of the log of the cyanide ion concentration. Instability of the potentiometric measurement was observed in all concentration ranges, especially in the low concentration range. Attempts to improve the electrode stability and potential drift were unsuccessful. Efforts using the specific ion electrode were abandoned for another procedure using gas chromatography.

A gas chromatograph procedure, which did not require bag samples for the collection of hydrogen cyanide and cyanogen, was investigated. This procedure used a chemical collection of cyanide ion in sodium or potassium hydroxide. Initially, the analysis was to be conducted by reacting chloramine-T with the trapped cyanide ion in an acid buffered solution to produce cyanogen chloride. Cyanogen chloride was then extracted by hexane and analyzed with an electron capture detector. The electron capture detector was chosen because of its high sensitivity and selectivity to halogenated compounds and relative insensitivity to hydrocarbons. Problems with impurities in the hexane caused broad peaks with an excessive analysis time. To eliminate the problem, the following items were tried:

1. Temperature program sequences

2. Column backflush

3. Column changes

    A. 6' X 1/4" O.D. glass column packed with 100/120 mesh Porapak QS
    B. 6' X 1/4" O.D. stainless steel column packed with 50/80 mesh Porapak Q
    C. 6' X 1/4" O.D. stainless steel packed with 7 percent Hallcomid M-18 on 90/100 mesh Anakrom ABS

4. Hexane purification with charcoal

5. Other extracting solvents (i.e., cyclohexane, etc.)

None of these proved to be satisfactory and long analysis times were the result.

A modification of the above procedure was tried by eliminating the hexane layer and conducting the analysis in the same manner as described above, except that the sample was placed in an air tight reaction vial with a 1 mℓ head space and a septum cap. A sample development period of 5 minutes was required. After vigorously shaking the vial for 5 seconds, 100 $\mu\ell$ of the head space was injected into the gas chromatograph. An electron capture detector was used for the analysis. As a result of this modification, a rapid analysis time was achieved. The finalized analytical procedure is included as an attachment of this report.

VALIDATION EXPERIMENTS

After selecting an analytical method, validation experiments were conducted to determine detector linearity, detection limits, injection repeatability, stability of reagents and sample, sampling parameters, etc. Once the validation experiments were complete, the procedure was considered ready for testing.

Collection parameters were determined with a series of experiments designed to check sample flow rates, absorbing reagent concentration, absorbing reagent temperature, impingers or fritted glass bubblers, and collection efficiency. All of these experiments were conducted with hydrogen cyanide.

The first experiments conducted were to determine the effects of stopper tip, sample flow rate, the reagent concentration on the collection efficiency. The results of these experiments are shown in Table 6. A set of three of the

TABLE 6. THE EFFECT OF STOPPER TIP AND ABSORBING
REAGENT CONCENTRATION ON COLLECTION EFFICIENCY AT ROOM TEMPERATURE

			$\mu g\ CN^-/ft^3$ sample					
			1.0 N KOH			0.1 N KOH		
Collection Device	Sample Flow	Run	1	2	3	1	2	3
impinger	1.0	1	93.47	7.71	1.55	50.02	7.08	6.21
impinger	1.0	2	65.71	9.26	2.61	60.13	6.06	0.00
impinger	1.0	3	74.28	6.38	0.00	49.92	6.16	5.48
		Avg	77.82	7.78	1.39	53.36	6.43	3.90
bubbler	1.0	1	11.44	0.00	0.00	4.64	1.40	2.73
bubbler	1.0	2	0.00	0.00	0.00	1.11	0.00	0.00
bubbler	1.0	3	0.00	0.00	0.00	2.57	0.00	0.00
		Avg	3.81	0.00	0.00	2.77	0.47	1.37
impinger	4.0	1	37.15	5.35	0.67	29.60	3.53	0.77
impinger	4.0	2	29.18	3.18	0.60	27.20	3.24	1.08
impinger	4.0	3	28.96	2.90	0.35	27.24	2.69	0.62
		Avg	31.76	3.81	0.54	28.01	3.15	0.82
bubbler	4.0	1	20.20	1.41	0.00	15.14	1.85	0.00
bubbler	4.0	2	25.30	2.96	3.52	7.42	0.85	0.00
bubbler	4.0	3	18.94	2.10	0.32	16.21	1.78	0.00
		Avg	21.48	2.16	1.28	12.92	1.49	0.00

same type collection devices (impinger or fritted glass tipped bubblers) were filled with 1.0 N or 0.1 N potassium hydroxide. A hydrogen cyanide calibration blend that contained a nominal 2 ppm concentration in a balance of nitrogen was passed through the absorbing reagent at 1.0 and 4.0 ℓ/min. Each experiment was repeated three times. All of these experiments were conducted in a special blending building, which was external to the main building. This building did not have the normal temperature controls within the building and the ambient temperature fluctuated with the weather. The room temperature ranged from about 15 to 30°C during the experiments.

After careful examination of the data, several trends can be observed. First, in all cases, more cyanide ion was collected with the stronger absorbing reagent. Secondly, more cyanide ion was trapped with the impinger than the fritted glass tipped bubbler. The possible reason for this was a flow restriction due to the fritted glass tip. Finally, the higher flow rate produced more consistent results with both concentrations of the absorbing reagent.

The next set of experiments took into account the results of the first set plus the effect of reagent temperature. Five sets of three impingers filled with 25 mℓ each of 1.0 N potassium hydroxide absorbing reagent were used. The sample flow rate was set at 4.0 ℓ/min. The first set of impingers was sampled at ambient room temperature (16-29°C) and a second set of impingers was sampled at ice bath temperatures. The sample collection efficiency for the ambient temperature experiments showed a high degree of variability. The collection efficiency for the first impinger was between 70 and 100 percent. At this temperature three impingers would be necessary to collect the entire sample even at low concentrations. With the ice bath, the first bubbler was sufficient to collect the entire sample as well as giving more consistent results. The data for these experiments is shown in Table 7.

Detector linearity was demonstrated for two cyanide ion concentration ranges. A linear response was observed in the 0 to 2 and the 0 to 10 μg CN^-/mℓ ranges. Table 8 and Figures 14 and 15 show the detector linearity. All samples are expected to be within this concentration range. If samples are obtained that are not in these regions, the samples will be diluted to a concentration which falls within the linear response of the detector.

Sample injection reproducibility is essential for an gas chromatography technique which does not involve the use of internal standard. To establish sample injection reproducibility, two nominal cyanide ion concentrations, 2.0 and 0.2 μg/mℓ , were used. Five separate samples of each concentration were developed and injected. The results are shown in Table 9.

Three separate experiments involving the sample storage and sample stability were also conducted. Three separate samples of known concentration were developed for the required time and injected as usual. At thirty-minute intervals, 100 μℓ of the remaining head space was also injected. The decay of the peak areas for a two-hour period is shown in Figure 16. Five separate samples of equal concentration were developed for varying lengths of time. The first sample was injected immediately, the second after 30 minutes, the third after 60 minutes, the fourth after 90 minutes, and the

TABLE 7. THE EFFECT OF ABSORBING REAGENT TEMPERATURE ON HCN COLLECTION EFFICIENCY

Date	Run	Absorbing Reagent Temperature °F	Absorbing Reagent Temperature °C	Time min	Flow ℓ/min	$\mu g\ CN^-/ft^3$ 1	$\mu g\ CN^-/ft^3$ 2	$\mu g\ CN^-/ft^3$ 3	$\mu g\ CN^-/ft^3$ Total	$\mu g\ CN^-/m^3$ 1	$\mu g\ CN^-/m^3$ 2	$\mu g\ CN^-/m^3$ 3	$\mu g\ CN^-/m^3$ Total	ppm CN^- 1	ppm CN^- 2	ppm CN^- 3	ppm CN^- Total
10/11/77	1	72	22	20	4.0	48.61	4.39	0.00	53.00	1716.6	155.0	0.0	1871.7	1.54	0.14	0.00	1.68
10/13/77	2	61	16	20	4.0	64.98	0.00	0.00	64.98	2294.7	0.0	0.0	2294.7	2.07	0.00	0.00	2.07
10/17/77	3	63	17	20	4.0	35.27	7.02	3.76	46.05	1245.5	247.9	132.8	1626.2	1.12	0.22	0.12	1.46
10/17/77	4	73	23	20	4.0	30.06	10.33	3.95	44.34	1061.6	364.8	139.5	1565.8	0.97	0.33	0.13	1.43
10/17/77	5	84	29	20	4.0	24.46	8.09	2.26	34.81	863.8	285.7	79.8	1229.3	0.80	0.26	0.07	1.13
					Avg	40.68	5.97	1.99	48.64	1436.7	210.7	70.3	1717.4	1.30	0.19	0.06	1.55
10/12/77	1	32	0	20	4.0	55.76	0.00	0.00	55.76	1968.1	0.0	0.0	2147.1	1.77	0.00	0.00	1.77
10/12/77	2	32	0	20	4.0	51.96	0.00	0.00	51.96	1834.9	0.0	0.0	1834.9	1.67	0.00	0.00	1.67
10/12/77	3	32	0	20	4.0	57.86	0.00	0.00	57.86	2043.3	0.0	0.0	2043.3	1.86	0.00	0.00	1.86
10/12/77	4	32	0	20	4.0	54.00	0.00	0.00	54.00	1907.0	0.0	0.0	1907.0	1.92	0.00	0.00	1.92
10/12/77	5	32	0	20	4.0	51.05	0.00	0.00	51.05	1802.8	0.0	0.0	1802.8	1.65	0.00	0.00	1.65
					Avg	54.13	0.00	0.00	54.13	1911.6	0.0	0.0	1947.2	1.77	0.00	0.00	1.77

TABLE 8. CALIBRATION CURVE LINEARITY AT SEVERAL CYANIDE CONCENTRATIONS

Test	Date	CN^- Conc. µg/mℓ	GC Attn	Sample height	Sample area	Background Corrected height	Background Corrected area
1	10/11/77	9.64	X256	45	4650	44	4600
		4.82	X256	26	2644	25	2594
		1.93	X256	11	1182	10	1132
		0.96	X256	5	583	4	533
		0.00	X256	1	50	0	0
2	10/12/77	9.64	X256	40	4102	40	4102
		4.82	X256	24	2448	24	2448
		1.93	X256	9	953	9	953
		0.96	X256	5	518	5	518
		0.00	X256	0	0	0	0
3	10/03/77	1.93	X64	80	7939	79	7816
		0.96	X64	42	4146	41	4023
		0.48	X64	19	1947	18	1824
		0.19	X64	8	817	7	694
		0.00	X64	1	123	0	0
4	10/04/77	1.93	X64	68	6813	68	6813
		0.96	X64	36	3538	36	3538
		0.48	X64	17	2027	17	2027
		0.19	X64	6	643	6	643
		0.00	X64	0	0	0	0

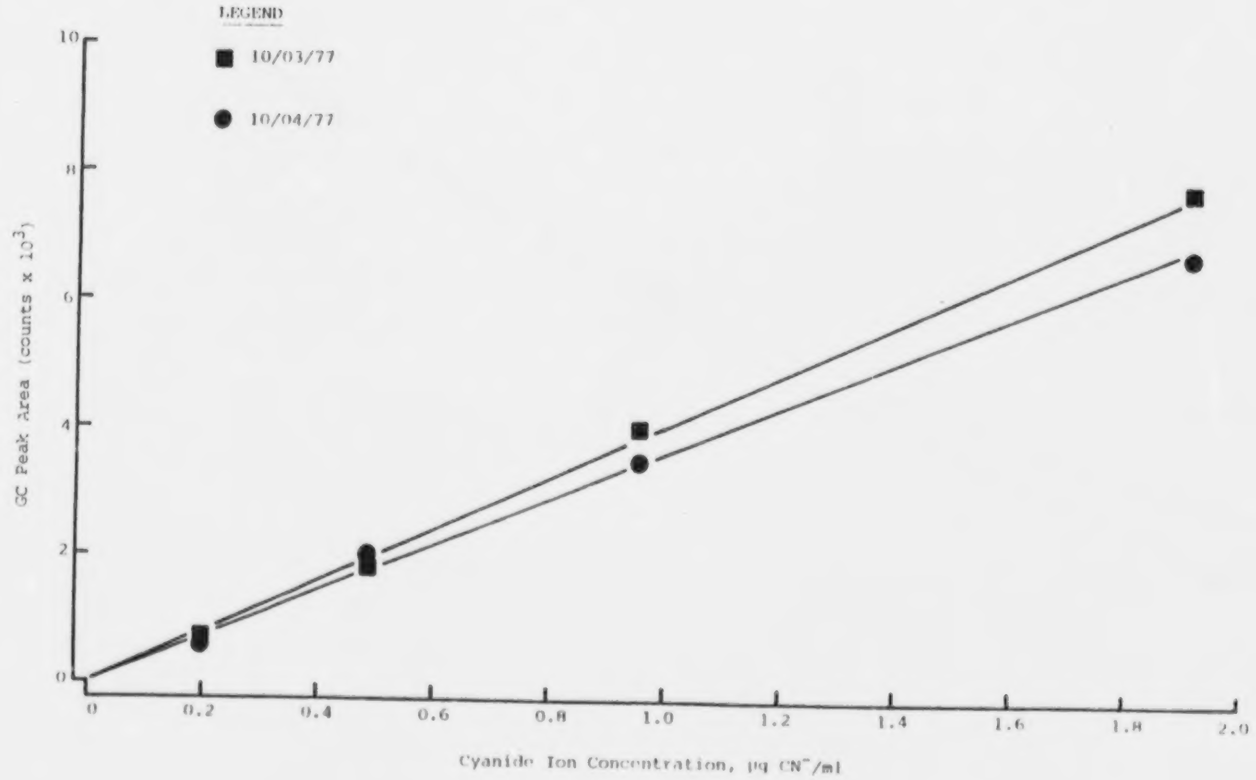


Figure 14. Total cyanide calibration curve at low concentrations (0-2 ppm).

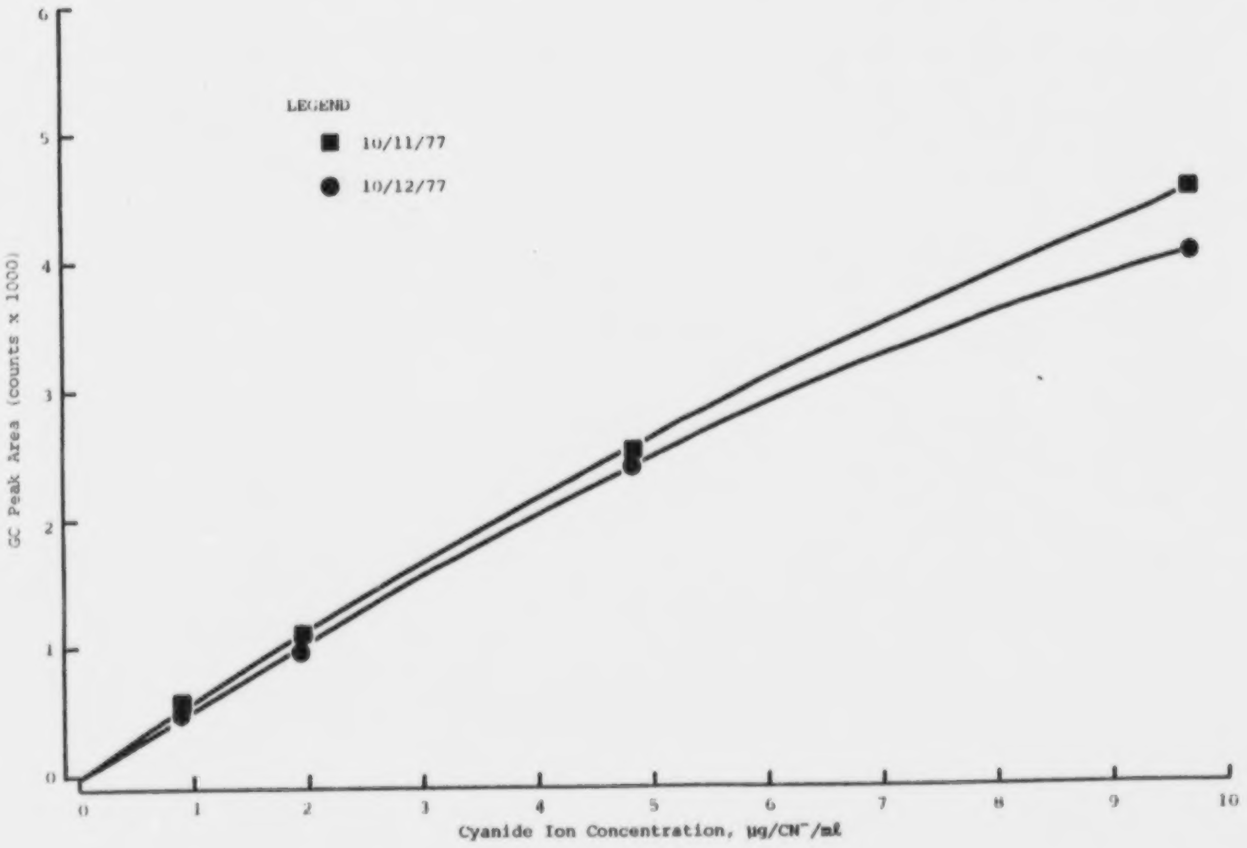
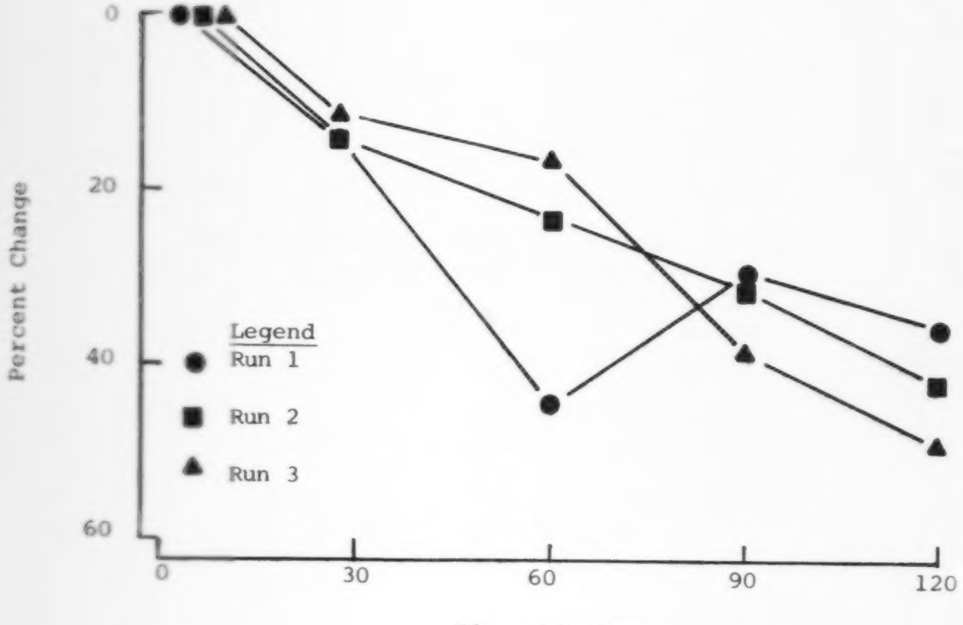


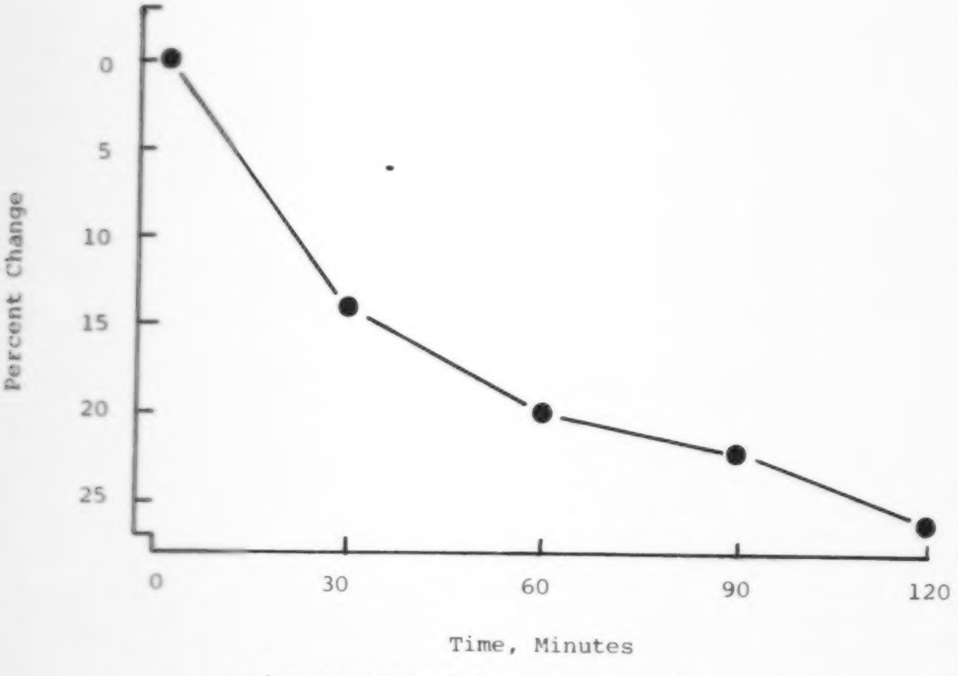
Figure 15. Total cyanide calibration curve at low concentrations (0-10 ppm).

TABLE 9. SAMPLE INJECTION REPEATABILITY FOR TWO CYANIDE CONCENTRATIONS

Sample	Nominal ppm	GC Attn	Peak Height	Peak Area
1	2.0	X256	62	6807
2	2.0	X256	60	6550
3	2.0	X256	61	6675
4	2.0	X256	61	6703
5	2.0	X256	63	6913
$\bar{x}$			61.4	6730
S_x			1.1	137.5
Cv			1.9	2.0
1	0.2	X32	66	6621
2	0.2	X32	70	7095
3	0.2	X32	68	6838
4	0.2	X32	65	6711
5	0.2	X32	64	6544
$\bar{x}$			66.6	6762
S_x			2.4	216.0
Cv			3.6	3.2



Sample decay with time



Five samples with varying development time

Figure 16. The effect of elapsed time on sample development.

fifth after 120 minutes. The sample decay, as a function of time, is also shown in Figure 16. In both cases, the concentration of cyanogen chloride in the head space is dependent on the length of time in which the sample was developed. The third experiment involves the effect of real exhaust samples that have been stored over a period of time. Sample storage stability is necessary when samples cannot be processed immediately or if confusing data is to be checked at a later date. A random sample was chosen and reprocessed periodically for 50 days. The results are shown in Figure 17. As a result, samples can be stored for a period of several weeks without adverse effects.

The freshness and stability of the reagents is also very important for the quantitative analysis of total cyanide. Solutions of both chloramine-T and the buffer were stored for various lengths of time. Samples developed with these stored solutions were found to be inferior to freshly prepared reagents. For these reasons, the reagents should be prepared daily.

Several ions were tested for interference with the production of cyanogen chloride or the production of other compounds with similar retention times in the column. Those ions tested were sulfate, phosphate, permanganate, nitrate, carbonate, chloride, bromide, cyanate, thiocyanate, and ammonium ions. The potassium salts of each of these ions were prepared in 100 ppm and 1 ppm concentrations in the presence of 4 ppm cyanide ion. The sulfate and nitrate salts of ammonium ion were then tried after the potassium salts of the sulfate and nitrate ions were found not to interfere. Aliquots of each were then developed for cyanogen chloride. Sulfate, phosphate, nitrate, carbonate, and ammonium ions showed no effect on the development of cyanogen chloride in the 100 ppm or 1 ppm ranges. Chloride, bromide, and permanganate ions produced little or no effect at low concentrations. At high concentrations, both bromide and permanganate ions decreased the concentration of cyanogen chloride produced. On the other hand, chloride ion increased the concentration. Cyanate and thiocyanate ions produced a positive interference at both concentrations. Apparently, these two ions also form a halide in the presence of chloramine-T with the same retention times as cyanogen chloride.

QUALIFICATION EXPERIMENTS

Qualification experiments for the total cyanide procedure were conducted with a Mercedes 240D. Hot FTP (23 minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel (18 inch diameter) injection + vehicle experiments. A cylinder containing 485 ppm hydrogen cyanide in balance nitrogen was used as the source for hydrogen cyanide. The flow of cyanide into the tunnel was regulated to give a concentration of 0.5 to 1 ppm hydrogen cyanide in the dilution tunnel.

The baseline emission rate for the Mercedes 240D was ~ 0.01 ppm. Injection of hydrogen cyanide into the tunnel without exhaust gave recoveries that ranged from 82 percent to 108 percent with an average of 98 percent (Table 10). The recovery of hydrogen cyanide in the presence of vehicle exhaust without a filter to remove particulate from the sampled exhaust gave recoveries that ranged from 68 to 84 percent with an average of 76 percent (Table 11). The recoveries ranged from 75-85 percent (Table 11) when a non-heated 0.5 μ Fluoropore filter was used to remove particulate from the sampled

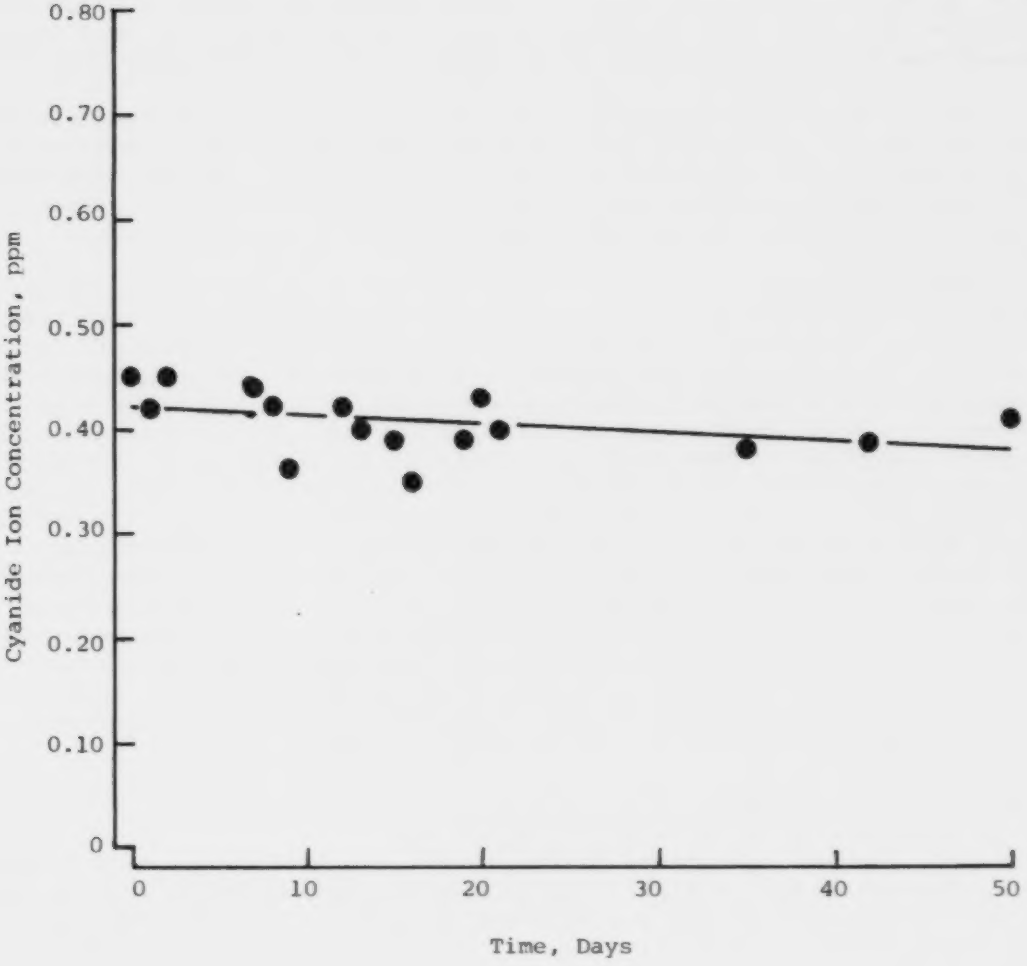


Figure 17. Time-sample decay curve.

TABLE 10. TOTAL CYANIDE GASEOUS RECOVERY BY DIRECT CVS INJECTION

Actual ppm Injected	Nominal Flow Rate, ft^3/min		Run	Sample	Calculated ppm HCN dilute	Observed ppm*	Percent Recovery HCN
	HCN Blend	CVS					
485	0.35	270	1	1	0.60	0.60	100
485	0.35	270	1	2	0.60	0.61	102
485	0.35	270	1	3	0.60	0.62	103
485	0.35	270	2	1	0.61	0.60	98
485	0.35	270	2	2	0.61	0.66	108
485	0.35	270	3	1	0.60	0.57	95
485	0.35	270	3	2	0.60	0.58	97
485	0.35	270	3	3	0.60	0.49	82
						Average	98 ± 8%

*Background subtracted from observed concentration (0.03 ppm)

TABLE 11. TOTAL CYANIDE RECOVERY FROM DILUTE EXHAUST WITHOUT FILTER OR WITH NON-HEATED FILTER

Actual ppm Injected	Run	Sample	Total Cyanide Conc. as HCN, ppm			Percent Recovery
			Calculated Amount	Observed	Corrected*	
			non-filtered			
485	1	1	0.60	0.42	0.41	68
485	1	2	0.60	0.47	0.46	77
485	2	1	0.61	0.50	0.49	80
485	3	1	0.62	0.53	0.52	84
485	3	2	0.62	0.44	0.43	69
					Average	76 ± 7%
			filtered/non-heated**			
485	4	1	0.60	0.46	0.45	75**
485	5	1	0.61	0.50	0.49	80**
485	6	1	0.62	0.54	0.53	85**
					Average	80 ± 5%

*Concentration corrected for background levels and vehicle baseline emissions

**Particulate removed from exhaust stream with non-heated 0.5 μ Fluoropore filter exhaust stream. Higher recoveries of 88-113 percent (average 99 percent) were obtained when a heated glass fiber filter (375°F) was used to remove particulate from the sampled exhaust stream. (Table 12).

TABLE 12. TOTAL CYANIDE RECOVERY FROM DILUTE EXHAUST WITH HEATED FILTER

Actual ppm Injected	Run	Sample	Total Cyanide Conc. as HCN, ppm Calculated Amount	Observed	Corrected*	Percent Recovery
485	1	1	0.54	0.61	0.58	107
485	1	2	0.54	0.54	0.51	94
485	1	3	0.54	0.64	0.61	113
485	1	1	0.55	0.54	0.51	93
485	1	2	0.55	0.54	0.51	93
485	1	3	0.55	0.61	0.58	105
485	1	1	0.57	0.53	0.50	88
485	1	2	0.57	0.58	0.55	96
					Average	99 ± 9%

---

*Concentration corrected for background levels and for vehicle baseline emissions

RESULTS AND CONCLUSIONS

The measurement of hydrogen cyanide and cyanogen in dilute exhaust can be conducted with a gas chromatography technique. Cyanide ion is trapped in a potassium hydroxide solution and reacted with chloramine-T to produce cyanogen chloride. Injection of the cyanogen chloride determines the concentration of cyanide ion in the sample. This procedure has a minimum detection limit of 0.01 ppm cyanide ion.

The effect of interfering ions in the absorbing reagent was investigated. The ions investigated included sulfate, phosphate, permanganate, nitrate, carbonate, chloride, bromide, cyanate, thiocyanate, and ammonium ions. Sulfate, phosphate, nitrate, carbonate and ammonium ions exhibited no effect on the cyanide ion concentration while chloride, bromide, and permanganate ions interfered only at high concentrations. High concentrations of chloride, bromide, and permanganate ions are not expected in dilute exhaust and the cyanide ion concentrations should not be affected by these ions. The presence of cyanate and thiocyanate ions affect the cyanide ion concentration, and therefore, the definition of total cyanide must take into account the possible existence and interference of these ions.

As a result of preliminary testing with real exhaust, it was discovered that two bubblers were necessary to efficiently trap the cyanide ion that was present in exhaust. Two factors which might necessitate the use of two bubblers instead of one are presented below. First, cyanogen has a much lower trapping efficiency than hydrogen cyanide in potassium hydroxide. This difference in trapping efficiency was discovered while naming high concentration cylinders which were to be used in the qualification experiments. Secondly, the temperature of the exhaust stream is somewhat higher than the temperature of the gases used in the determination of the sampling parameters. The same breakthrough can be expected as with ambient conditions because the sample gas is not cooled effectively by only one impinger in the ice bath. Two impingers are therefore necessary for complete sample recovery. The final sampling parameters are listed below:

1. 25 mℓ of 1.0 N potassium hydroxide absorbing reagent.
2. Absorbing reagent held at ice bath temperature (0°C-5°C).
3. Sample flow rate of 4.0 ℓ/min.
4. Impingers rather than fritted glass bubblers.
5. Two impingers in series.

These parameters were sufficient to collect a sample from dilute exhaust within the detection limits of the procedure.

The measurement of hydrogen cyanide in the presence of cyanogen is difficult if wet chemical techniques are used. In clear or dark Tedlar bags, hydrogen cyanide is stable for at least 60 minutes, if the humidity within the bag is not too high. High humidity increases the possibility of hydrogen cyanide condensation on the walls of the bag. Cyanogen, on the other hand, cannot be quantitively stored in the presence of exhaust. Therefore, bag samples for the measurement of cyanogen is only a qualitative tool which can determine if cyanogen is actually produced in exhaust.

Injection repeatability, sample stability, and sample storage are three basic requirements for most analytical methods. The injection repeatability is well within the expected nominal 5 percent limit for a gaseous syringe injection. The concentration of cyanogen chloride within the head space is dependent upon the volume of the head space, the room temperature, and concentration of cyanide ion present. A 5 mℓ reaction vial with a septum cap is used in the analysis. A total of 4 mℓ of the various solutions is added to this vial. When the vial is tightly capped, a 1 mℓ head space remains above the solution. This head space remains constant unless the vial is not tightly capped or the wrong volumes of reagents are pipetted into the vial. Cyanogen chloride obeys Henry's law in the head space. Henry's laws states that the mass of a slightly soluble gas that dissolves in a definite mass of a liquid at a given temperature is very nearly proportional to the partial pressure of that gas. Henry's law holds for gases which do not chemically unite with the solvent and is obeyed by a variety of gases in dilute solutions and all gaseous solutions at the limit of extreme dilution. The sample stability is maintained for only a short time after complete development. The sample may be stored undeveloped in the potassium hydroxide absorbing reagent for at least three weeks.

When a heated filter is used to remove particulate from the sampled exhaust stream, 99 percent of the hydrogen cyanide injected into the dilution tunnel can be recovered. When a non-heated filter or no filter is used, only 76-80 percent of the cyanide can be recovered. From these experiments, it is recommended that a heated filter be used in the sampling system to increase recoveries and to prevent contamination of the sampling system.

This procedure provides a rapid and sensitive method for the analysis of total cyanide in dilute exhaust. The analysis of a single sample requires two minutes for reagent addition, five minutes for sample development, and five minutes for the total peak elution time. Total sample processing time is twelve minutes per sample. The simplicity and ease of analysis makes this procedure ideal for repetitive analysis.

SECTION 4

INDIVIDUAL HYDROCARBON PROCEDURE

LITERATURE SEARCH

The eight individual hydrocarbons (methane, ethane, ehtylene, acetylene, propane, propylene, benzene, and toluene) have been measured by innumerable techniques. One of the most efficient techniques for the individual determination of all of these compounds in a single analysis is with gas chromatography. Because of its efficiency, this means of analysis was selected over any of the other available techniques.

Hydrocarbons are of interest as exhaust components because of their potential for photochemical smog formation. Hydrocarbons are placed into four classes according to their participation in atmospheric reactions. Methane, ethane, acetylene, propane, and benzene are placed in Class I, the non-reactive category. The Class II reactive category includes the C_4, and higher paraffins, while the Class III reactive category encompasses all of the aromatics except benzene. The olefins are placed in the Class IV reactive category. When olefins such as ethylene react with ozone

$$O_3 + H_2C = CH_2 \rightarrow H_2C = O + \dot{H}O + H\dot{C}O$$

the precursors of photochemical smog are formed. These free radicals then participate in other atmospheric reactions that result in oxidant formation.

Dimitriades and Seizinger (8) proposed a three-column system capable of analyzing at least 22 hydrocarbons. Two packed columns were required to resolve the C_1 and C_2 hydrocarbon components and an open tubular column was used to resolve the other components. The complete analysis consisted of two different sample loop sizes. This procedure was considered time consuming and the number of compounds to be analyzed was excessive.

Papa et al (9) presented a procedure for the analysis of C_1 through C_{12} hydrocarbons in automotive exhaust. This dual column system consisted of a packed column with a mixture of stationary phases for the resolution of C_1 and C_2 hydrocarbons and an open tubular column. About 200 individual peaks were obtained from the method. This procedure also required two sample loop injections. Excessively low temperatures were required for resolution of C_1 and C_2 hydrocarbons with this analytical system.

Klosterman and Sigsby (10) proposed a simple analytical system for the determination of hydrocarbons according to their potential for photochemical smog formation. A flame ionization analyzer was used in their work, though this technique did not employ the use of a gas chromatograph. A column similar to that used by Klosterman and Sigsby was used to scrub the oxygenated hydrocarbons and olefins from benzene and toluene by Black et al (11). This method utilizes four packed analytical columns for the resolution of the desired compounds. Methane, ethane, ethylene, acetylene, propane, and propylene are resolved with the first two columns; and benzene and toluene are resolved with the other two. As with the other procedures, two sample loops are required for the combined analysis of paraffins, olefins, and aromatic hydrocarbons. This procedure was also designed as a simple and inexpensive method for the determination of smog related compounds. Table 13 lists the compounds of interest, along with chemical formulas, boiling and melting points, synonyms, and molecular weights.

PROCEDURAL DEVELOPMENT

The gas chromatogarph procedure that will be used for the determination of the individual hydrocarbons is similar to the procedure used by Black et al (11) and consists of a four column system that is capable of resolving eight individual hydrocarbons. Columns I and II in the system consist of an 8' x 18" stainless steel tube packed with 80/100 mesh Porapak Q and a 4' x 1/8" Teflon column packed with 35/60 mesh type 58 silica gel, respectively. Column III consists of 15' x 1/8" stainless steel tube packed with 15 percent, 1, 2, 3-tris(2-cyanoethoxy) propane on 60/80 mesh Chromosorb PAW; and Column IV consists of a 2' x 1/8" stainless steel tube packed with 40 percent mercury sulfate ($HgSO_4$) and 20 percent sulfuric acid (H_2SO_4) on Chromosorb W. Columns II, III, and IV are used isothermally and Column I undergoes a temperature program sequence. The primary purpose of Column I is to resolve methane from air, while Column II resolves C_2 and C_3 hydrocarbons. Columns III and IV resolve benzene and toluene from the other aromatics, paraffins, olefins, acetylenes, and oxygenated hydrocarbons. Three timers, four solenoid valves, and five six-port gas sampling valves are required to accomplish the complicated sample flow through the columns. When exhaust from diesel powered vehicles is analyzed, higher molecular weight hydrocarbons have been found to interfere with the analysis. The compounds can be effectively removed by simply passing the exhaust sample through an ice trap before it enters the analytical system. The actual analytical procedure is included as an attachment to this report.

VALIDATION

This gas chromatographic procedure has been used with much success on a variety of projects. The validation of this procedure consists of the injection repeatability for all eight components of the calibration blend and bag sample stability. All other parameters were determined from previous experience with this analytical procedure.

The injection repeatability for the individual hydrocarbon procedure was conducted on two separate occasions. Table 14 shows the data accumulated on each occasion. The injection repeatability for the two 10 mℓ sample loops is not greater than ±2 percent.

TABLE 13. IMPORTANT FACTS ON INDIVIDUAL HYDROCARBONS

Compound	Formula	Molecular Weight	Melting Point	Boiling Point	Synonyms
Methane	CH_4	16.04	-182.48	-164	marsh gas, methyl hydride
Ethylene	C_2H_4	28.05	-169.15	-103.71	ethene, elayl, olefiant gas
Ethane	C_2H_6	30.07	-183.3	- 88.63	bimethyl, dimethyl, methylmethane, ethyl hydride
Acetylene	C_2H_2	26.04	- 80.3	- 75	ethyne, ethine
Propane	C_3H_8	44.11	-189.69	- 42.07	dimethylmethane, propyl hydride
Propylene	C_3H_6	42.08	-185.25	- 47.4	propene, methylethylene, methylethene
Benzene	C_6H_6	78.12	5.5	80.1	benzol, phene, cyclohexatriene
Toluene	C_7H_8	92.15	- 95	110.6	methylbenzene, phenylmethane, toluol, methacide

TABLE 14. INJECTION REPEATABILITY ON TWO SEPARATE OCCASIONS

Individual Peak Area, Relative Counts (Test 1)

Injection	Methane	Ethylene	Ethane	Acetylene	Propane	Propylene	Benzene	Toluene
1	7283	10097	[illegible]	12034	14809	15569	13897	15348
2	7527	10467	[illegible]	[illegible]	15092	15724	14015	15576
3	7792	10621	10029	12083	15352	16152	1367	15466
4	7566	10479	9892	[illegible]	14825	15910	13877	
5	7585	10495	9900	12675	15016	15899	13834	15478
6	7387	10300	9690	12398	14925	15441	14041	15576
7	7700	10575	9994	12753	15147	15931	14042	15780
8	7455	10307	9724	12460	14702	15629	14066	15799
9	7680	10493	9878	12624	14933	15842	14049	15459
10	7618	10481	9885	12714	14996	15857	13943	15783
Average	7559.30	10431.50	9847.20	12563.40	14979.70	15795.40	13933.10	15584.33
Standard Deviation, S_x	152.98	154.55	[illegible]	224.85	187.42	206.83	125.31	166.20
Coefficient of variation, C_v	2.02	1.48	[illegible]	1.79	1.25	1.31	[illegible]	1.07

Individual Peak Area, Relative Counts (Test 2)

Injection	Methane	Ethylene	Ethane	Acetylene	Propane	Propylene	Benzene	Toluene
1	8593	11893	10953	14803	15705	17867	16466	18646
2	8633	11937	11011	14992	15912	18020	16604	18537
3	8602	11993	11067	15139	15722	17818	16553	18735
4	8640	11885	10977	15170	15775	17926	16409	18479
5	8702	12022	11113	15371	15825	17850	16267	18530
6	8561	11900	10946	15252	15879	17955	16433	18562
Average	8622	11938	11015	15121	15803	17906	16455	18565
Standard Deviation, S_x	48.59	57.20	[illegible]	200.07	83.77	75.16	118.21	87.95
Coefficient of variation, C_v	0.56	0.48	[illegible]	1.32	0.53	0.43	[illegible]	0.47

The bag sample stability experiment was conducted on a random sample from an emissions test. The sample was collected during the driving cycle and analyzed immediately afterward. This sample was then reprocessed periodically for several days. A bag sample of the calibration standard and a bag sample of exhaust doped with the calibration standard were also processed periodically. The time-sample decay curve for each compound is shown in Figures 18, 19 and 20. The sample integrity can be preserved for approximately five days.

QUALIFICATION EXPERIMENTS

The analysis of individual hydrocarbons in dilute exhaust has previously been conducted on many projects. On the request of the Project Officer, no qualification experiments were conducted with the CVS for this procedure. Also, long term experience with this procedure has given an insight into the sample integrity for the complete analytical system.

RESULTS AND CONCLUSIONS

The measurement of individual hydrocarbons in dilute exhaust is conducted with a gas chromatography technique. Tedlar bags are filled with dilute exhaust during each driving cycle. Analysis of the bag sample requires a complicated system of four analytical columns with backflush and temperature program capability. Sample concentrations are determined by comparison to a calibration blend of all eight hydrocarbons. The minimum detectable limit is 0.1 ppmC to 0.2 ppmC. The higher molecular weight compounds approach the higher minimum detectable limit.

Injection repeatability and bag sample stability were demonstrated for the system. The largest injection variability was with methane and acetylene and the smallest was with benzene and toluene. A 2 percent variability can be expected for the six compontents of the first sample loop and first two columns (C_1 - C_3), and a 1 percent variability can be expected for the second sample loop and second two columns (benzene and toluene). This agreement is much better than can be expected of a syringe sample injection. The bag sample stability shows that dilute exhaust samples will be stable for about five days. Only propylene, benzene and toluene were shown to have a large decrease in concentration over a period of time in exhaust. With the standard only sample, all compounds showed the same decrease in concentration. A leak in the bag is suspected as a cause of this drastic change in concentration. However, even with a leak in the bag, the sample concentration is stable for about five days. Samples must be analyzed before this time to maintain confidence in the sample concentrations obtained. Otherwise, the sample integrity is lost due to sample decay, bag leakage, and/or permeation through the walls of the bag.

This procedure provides an effective means for the analysis of individual hydrocarbons in dilute exhaust. A single bag requires about four minutes to purge the sample loops, 23 minutes for total peak elution, and five minutes to cool the oven temperature back to room temperature and reset the instrumentation. The total analysis time per sample is about 32 minutes. The auto-

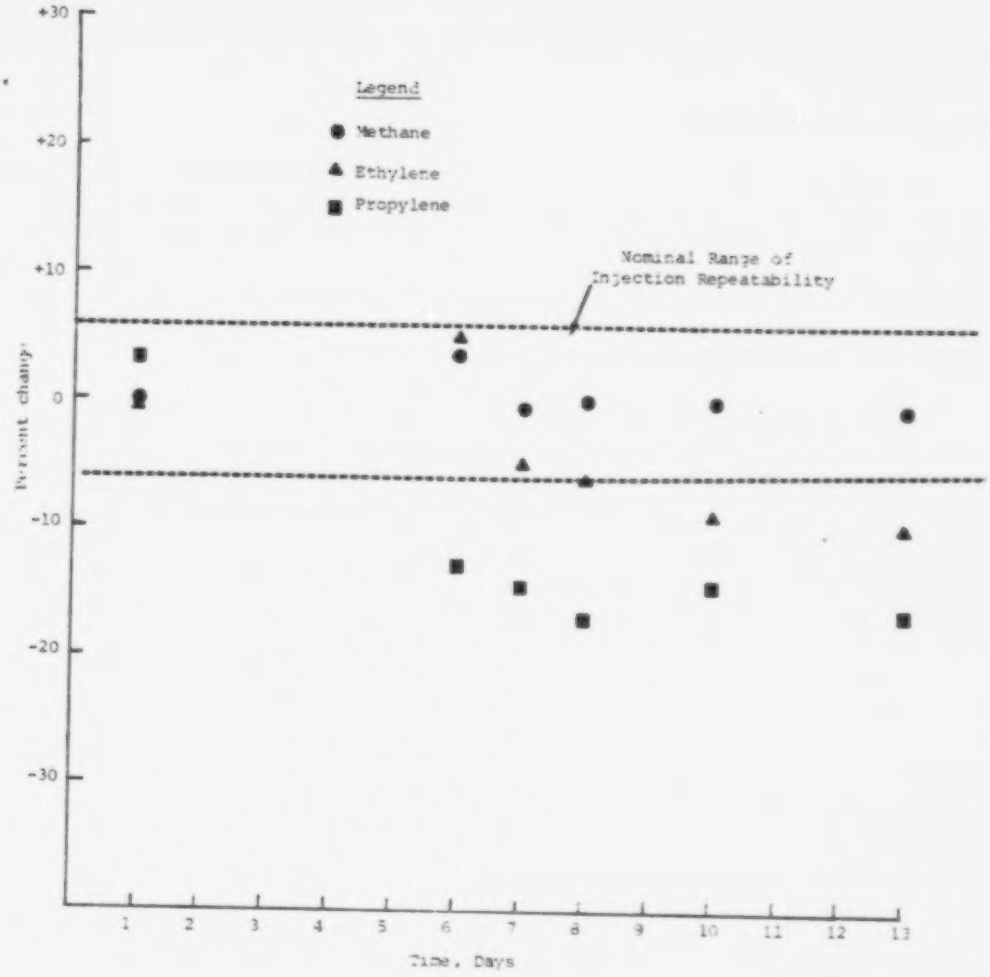


Figure 18. Time-sample decay curve (exhaust only).

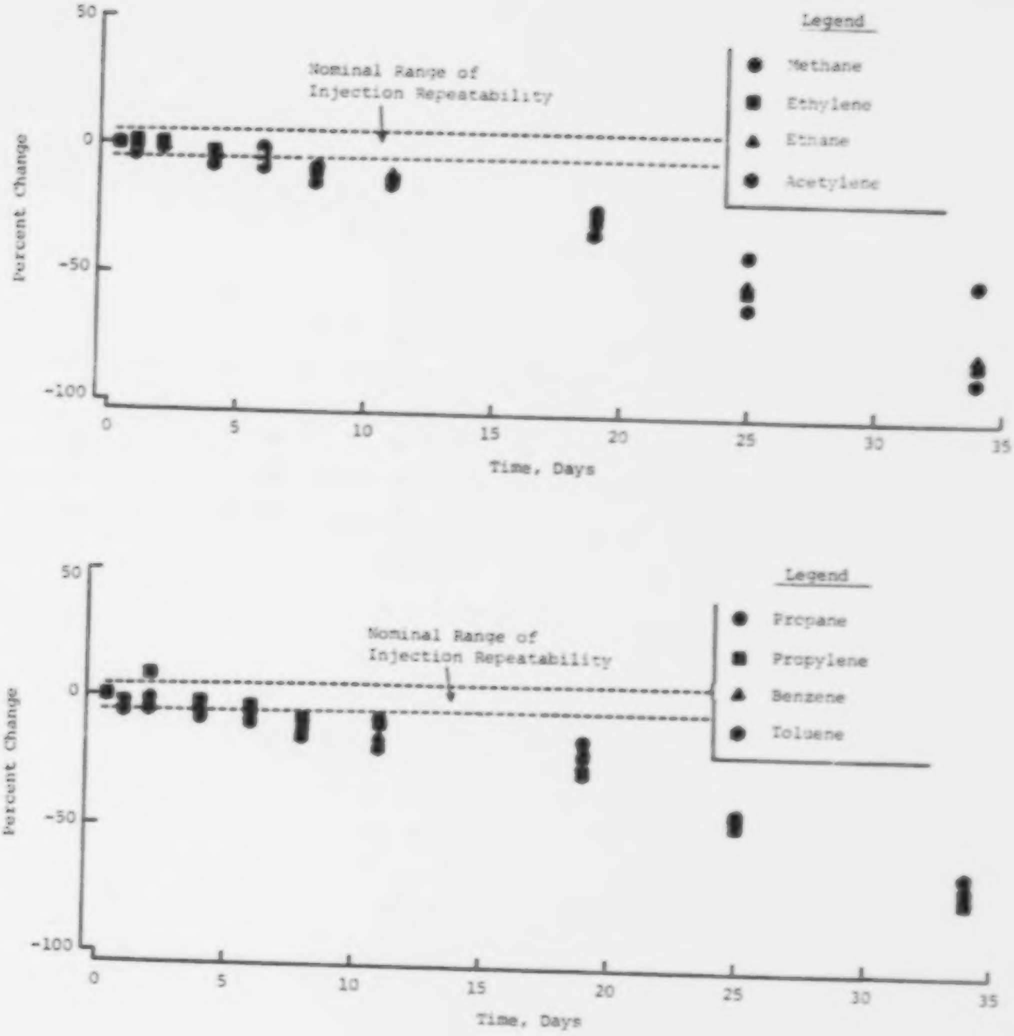


Figure 19. Time-sample decay curve (standard only).

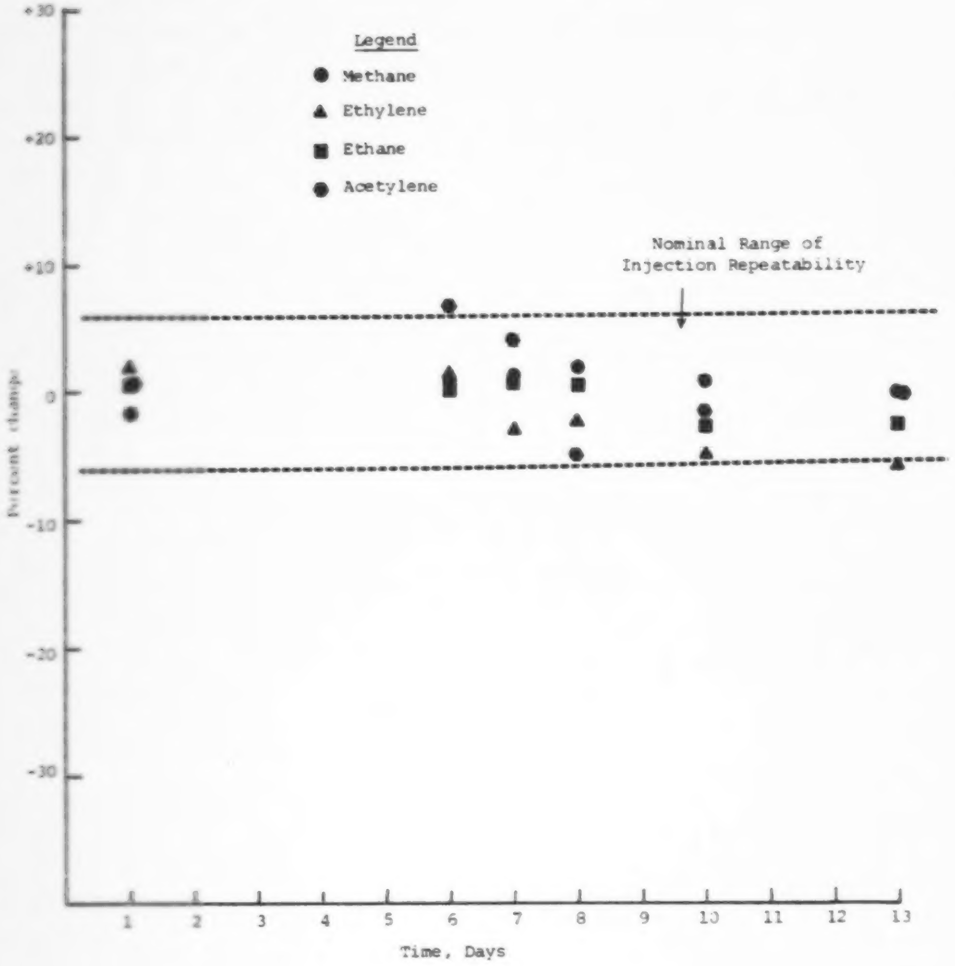


Figure 20. Time-sample decay curve (exhaust + standard).

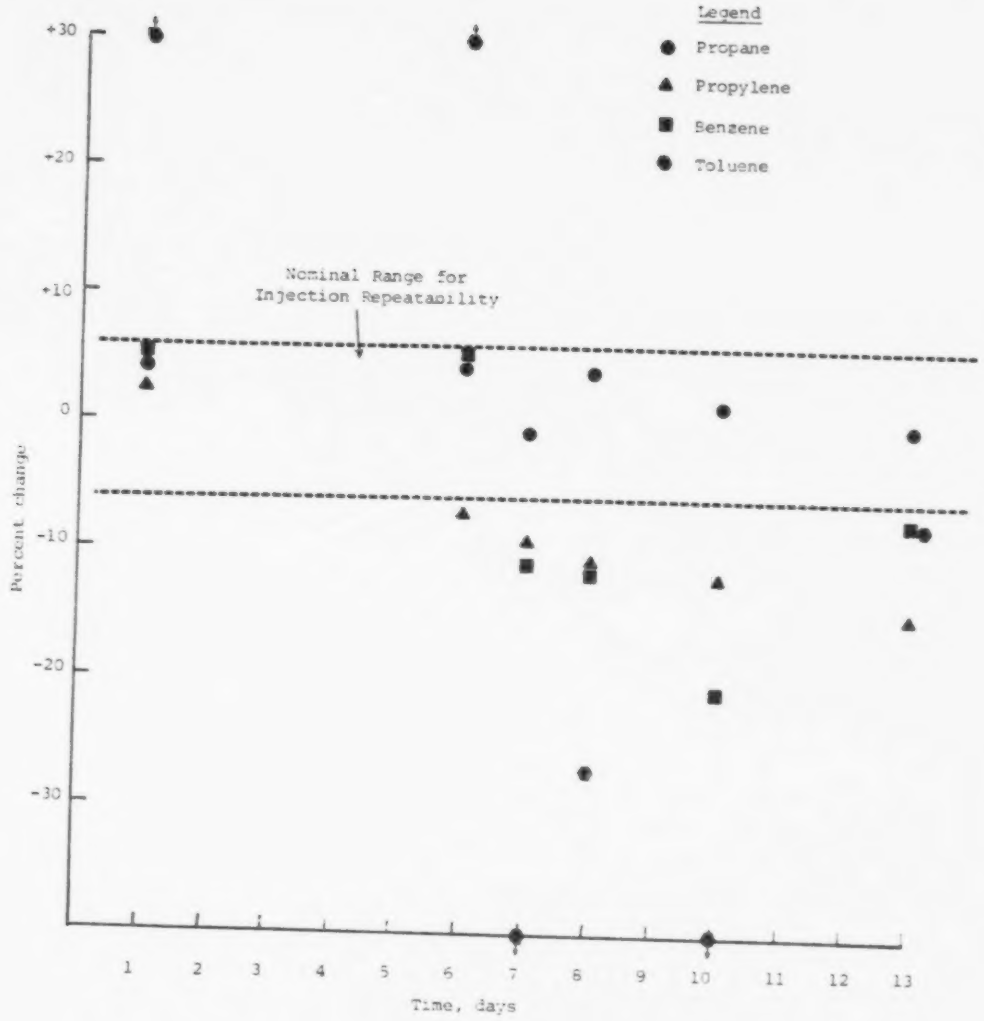


Figure 20 (Cont'd). Time-sample decay curve (exhaust + standard).

mated system provides a simplified operation for an otherwise complicated procedure and enables routine analysis for a large quantity of samples.

SECTION 5

ORGANIC AMINE PROCEDURE

LITERATURE SEARCH

The individual amines that are included in this analysis are monomethylamine, dimethylamine, monoethylamine, trimethylamine, diethylamine and triethylamine. The chemical formulas, molecular weights, boiling points, freezing points, and synonyms for these low molecular weight aliphatic amines are presented in Table 15. In general, these amines have a fish-type odor at lower concentrations, but more of an ammoniacal odor at higher levels. The 1968 American Conference of Governmental Industrial Hygientists has recommended a threshold limit value of 10 ppm.

The measurement of individual low molecular weight amines has been conducted using a variety of gas chromatograph techniques. Hoshike (13,14) reported gas chromatographic separation of lower aliphatic amines in the free form and as their Schiff base derivatives. A glass column was employed to provide a separation of 11 amines using temperature programming and a thermal conductivity detector. This work was directed toward achieving a satisfactory separation rather than being concerned with minimum detection limits. Sze (15), et al reported separation of methyl amines, ammonia, and methanol using a mixture of tetrahydroxyethylethlenediamine and tetraethylenepentamine. O'Donnel and Mann (16) used Dowfax 9N9, Carbowax 400, and Carbowax 20M to separate mixtures of aliphatic amines, aromatic amines, and aliphatic amines. This work was performed using synthetic blends on a gas chromatograph with a thermal conductivity detector. McCurdy and Meiser (17) used a gas chromatograph with a flame ionization detector to determine fatty amines in trace quantities. The fatty amines were converted to trifluoracetyl derivatives, providing a sensitivity of 0.05 ppm fatty amine in water.

Smith and Waddington (18) used aromatic polymer beads to seperate a wide range of aliphatic amines. Peak tailing was found to exist because of two types of active sites on the polymer: simple acidic sites which can be neutralized by treatment with base, and metal ions which must be deactivated by addition of an involatile complexing agent. Glass columns were used in a gas chromatograph with a flame ionization detector. Synthetic blends ranging from C_1-C_6 were separated and analyzed using this approach. In another study Carbopak B/4 percent Carbowax 20 M/0.8 percent KOH (19) and 28 percent Pennwalt 223/4 percent KOH (20) have been reported to give satisfactory separations of lower aliphatic amines.

Analysis of amines as derivatives has been shown to be a valuable analytical tool to determine trace quantities (21). Thirteen different deri-

TABLE 15. LIST OF INDIVIDUAL ORGANIC AMINES INCLUDED IN THE EMISSIONS CHARACTERIZATION INVENTORY

Name		Carbon No.	Chemical Formula	Molecular Weight	Boiling Point, °C	Freezing Point, °C	Synomyms
Monomethylamine	(12)	1	CH_3NH_2	31.058	-6.32	-93.5	Methylamine, aminomethane
Monoethylamine	(12)	2	$C_2H_5NH_2$	45.085	16.58	-81.0	Ethylamine, aminoethane
Dimethylamine	(12)	2	$(CH_3)_2NH$	45.085	6.88	-92.19	None
Trimethylamine	(5)	3	$(CH_3)_3N$	59.112	2.87	-117.08	None
Diethylamine	(5)	4	$(C_2H_5)_2NH$	73.14	56.3	-50.	None
Triethylamine	(5)	6	$(C_2H_5)_3N$	101.19	89.3	-114.7	None

vatives were evaluated in terms of FID and ECD response characteristics. This work was limited to primary amines, and under optimum conditions amines down to 10 picograms could easily be quantified using an ECD detector. Clark and Wilk (22) used an ECD to evaulate the properties of halogenated amine derivatives. No increase in the sensitivity for the trifluoroacetyl amine derivatives using ECD was observed.

Mosier (23), et al quantitatively measured aliphatic amines volatilized from cattle feedyards. Direct gas chromatograph injection of acid solutions and GC separation of the pentafluorobenzoyl derivatives of the malodorous volatiles were used in identification. The derivatized amines were analyzed using a gas chromatograph equipped with an electron capture detector.

Methylamine and ethylamine were detected in irradiated beef by Burks (24), et al. Several techniques, including colorimetric paper chromatography and gas chromatography, were used in quantifiying results. Gas chromatographic determination of free mono-, di-, and trimethylamines in biological fluids were performed by Dunn (25), et al. A flame ionization detector was used to quantitatively separate the lower aliphatic amines. Separation of mono-, di-, and trimethylamine from extracts of fish tissue was achieved by Gruger (26).

Andrea (27), et al developed a precolumn inlet system for the gas chromatographic analysis of trace quantities of short-chain aliphatic amines. Losses inherent in the collection and direct gas chromatograph analysis of field air samples containing volatile amines necessitated an indirect analytical scheme. A Teflon tube (3" x 5/16" OD) was filled with 20/30 mesh Ascarite and placed in the injector inlet of the gas chromatograph. Samples were collected in dilute sulfuric acid and aliquots were injected into the pre-column of the GC. Release of the free amines was found to be sufficiently reproducible for quantification of results. This technique avoided the problems encountered by Umbreit (28), et al, and Hardy (29) when using base loaded columns to analyze acidified aqueous solutions of amines from fish. The in situ release of the free amines from their salts produced a chromatographic column that changed with every injection. In addition, the column had a very short usable lifetime and lacked reproducibility after extended use.

Bowen (30) described a gas chromatograph procedure for the analysis of aromatic amines using an adsorption technique. Quantitative adsorption and desorption of aromatic amines using Tenax GC was demonstrated at the nanogram level. Samples were pulled through the Tenax GC trap for specific sampling periods, thermally desorbed at 250°C, and analyzed in a GC with a FID. The author recommended use of a NPD to increase sensitivity for aromatic amines on the tail of hydrocarbon solvents and eliminate venting the solvent.

PROCEDURAL DEVELOPMENT

From the results of the literature search it was determined that the analysis of the amines should be conducted by the use of gas chromatography. A Perkin-Elmer 3920B gas chromatograph was dedicated for this purpose. This instrument has a dual/differential electrometer and has linear temperature programming capabilities along with a sub-ambient oven accessory. The instrument has been equipped with a flame ionization detector (FID), a nitrogen phosphorus detector (NPD), and an electron capture detector (ECD) and can be connected to a chemiluminescent detector. Of the specialty detectors available for the analysis of the amines, the NPD appeared to be the prime candidate and initial work was carried out using this detector. Because the amines are notorious for tailing and reacting with metal sites, a glass lined heated injector port and a glass interface were installed so that with the use of a glass column, the system would be glass throughout.

Lecture bottles of methylamine, dimethylamine, trimethylamine, and ethylamine, along with pure liquids of diethylamine and triethylamine, and a Tracor Model 412 Permeation Calibration System containing permeation tubes of all six amines were used as sources of the organic amines in the procedural development experiments. These sources allowed a method for preparing blends of varing concentrations of the organic amines.

Several column packing materials (all were developed especially for the analysis of amines) and column lengths were evaluated to determine which could provide the best peak separation with the shortest analysis time. The columns evaluated included: 12' x 1/4" glass columns packed with 28 percent Pennwalt 223 amine packing, a 6' x 4 mm (id), 6' x 2 mm (id) and a 12' x 1/4" glass column packed with 4 percent Carbowax 20 M and 0.8 percent KOH on Carbopak B, and a 6' x 4 mm (id) glass column packed with 2 percent KOH on Chromasorb 103. Several column temperatures, programming rates, and carrier flow rates (helium) were tried for each of the columns.

The best separation was accomplished using the 4 percent Carbowax 20 M and 0.8 percent KOH on Carbopak B packing material in the 6' x 4 mm (id) glass column. This column would only partially separate diemthylamine and ethylamine under conditions which gave very broad peaks at long retention time. In order to increase sensitivity and shorten the analysis time an initial temperature of 130°C was chosen. At this temperature, the dimethylamine and ethylamine coalesce into a single sharp peak, and the analysis time is under 30 minutes.

The FID, NPD, and chemiluminescent detector were evaluated as detectors for the organic amines. The NPD was more sensitive than either the FID or the chemiluminescent detector. Also the NPD is only sensitive to compounds containing both carbon and nitrogen, eliminating many interferences that would be present using the FID.

In order to analyze automobile exhaust for the organic amines, it was found necessary to concentrate the amines in a trap or an absorbing reagent to obtain enough sample for the satisfactory analysis. Two collection procedures were evaluated, one in which the amines are collected in a trap filled with 1 gram Tenax-GC packing material, and another in which the amines are collected by bubbling the amines through an acid solution. There was some breakthrough of the amines through the Tenax-GC traps even at liquid nitrogen temperatures. Bubbling the amines through an acid solution proved to be the superior method for collecting the amines.

A sulfuric acid solution was found to effectively trap the amines at room temperature. To release the amines from the sulfuric acid solution into the GC column, an Ascarite loaded precolumn was installed into the injector block of the GC. This precolumn was found to work very well in releasing the amines into the GC column; however, the lifetime of the precolumn was found to vary from one injection to several hundred. The 4 percent Carbowax 20 M and 0.8 percent KOH on Carbowax B packing material in the GC column was designed to be used with aqueous solutions and proved to be satisfactory when used with aqueous sulfuric acid solutions.

The usefulness of the precolumn was usually terminated by the aqueous injections temporarily dissolving the Ascarite and the Ascarite redrying to form a plug, thereby preventing the sample from entering the column. Some time was spent on trying to determine why some precolumns lasted for only one injection while others for several hundred, but the results were inconclusive.

Poor injection repeatability resulted from a variety of problems. These problems included previous GC injection history, glass syringe purging technique, precolumn conditioning, and column effects. Because of the problems mentioned above, and alternate method of analysis was evaluated. This method consisted of collecting the organic amines in glass impingers using dilute sulfuric acid, converting the trapped amines to their pentafluorobenzoyl chloride derivatives, and analyzing for these derivatives using a gas chromatograph equipped with an electron capture detector. It was hoped that this method would (1) convert the amines to stable derivatives which would improve sample injection repeatability, and (2) provide improved detection limits with an electron capture detector.

This alternate procedure was found to be unsuitable for the detection of amines at the ppb levels. Tertiary amines (trimethyl- and triethylamine) cannot be detected by this procedure, and the secondary amines (dimethyl- and diethylamine) had a low sensitivity that made detection in the ppb range almost impossible. The peak areas of the primary amines (methyl- and ethylamine were found to be time dependent. The GC peak areas of the methyl- and ethylamine derivatives were plotted against the time they were allowed to stand after initial mixing of the reagents to produce the derivatives. The mixing procedure is included in Table 16. The standing time includes 2 minutes of vigorous shaking (1 minute for the 1 minute test) plus any remaining time the mixture was allowed to stand at room temperature before injecting into the GC. The effect of elapsed time on peak area is shown in Figure 21. This figure shows a rapid increase in peak area followed by a rapid decrease in the area. In order to obtain reproducible data at ppb levels, the injection time after mixing can vary by only seconds. Under normal operating conditions this would not be possible. Because of the time limitation, the procedure was abandoned for the quantitative analysis of the organic amines.

TABLE 16. MIXING PROCEDURE FOR PREPARATION OF PENTAFLUORABENZOYLAMINE DERIVATIVES*

1. Pipette 1.0 mℓ of 0.01 N sulfuric acid containing 94 ppb methylamine and 220 ppb ethylamine into a 10 mℓ reacti-vial.
2. Pipette 3 mℓ of toluene into reacti-vial.
3. Pipette 1 mℓ of pentafluorobenzoyl chloride (PFBC) solution (50 μg PFBC in 100 mℓ toluene) into reacti-vial.
4. Pipette 1 mℓ of 10 percent aqueous potassium hydroxide solution into reacti-vial.
5. Shake and allow to stand for X minutes.

---

* General procedure from private communication with Arvin R. Mosier, USDA, ARS, P.O. Box E, Fort Collins, Colorado 80521

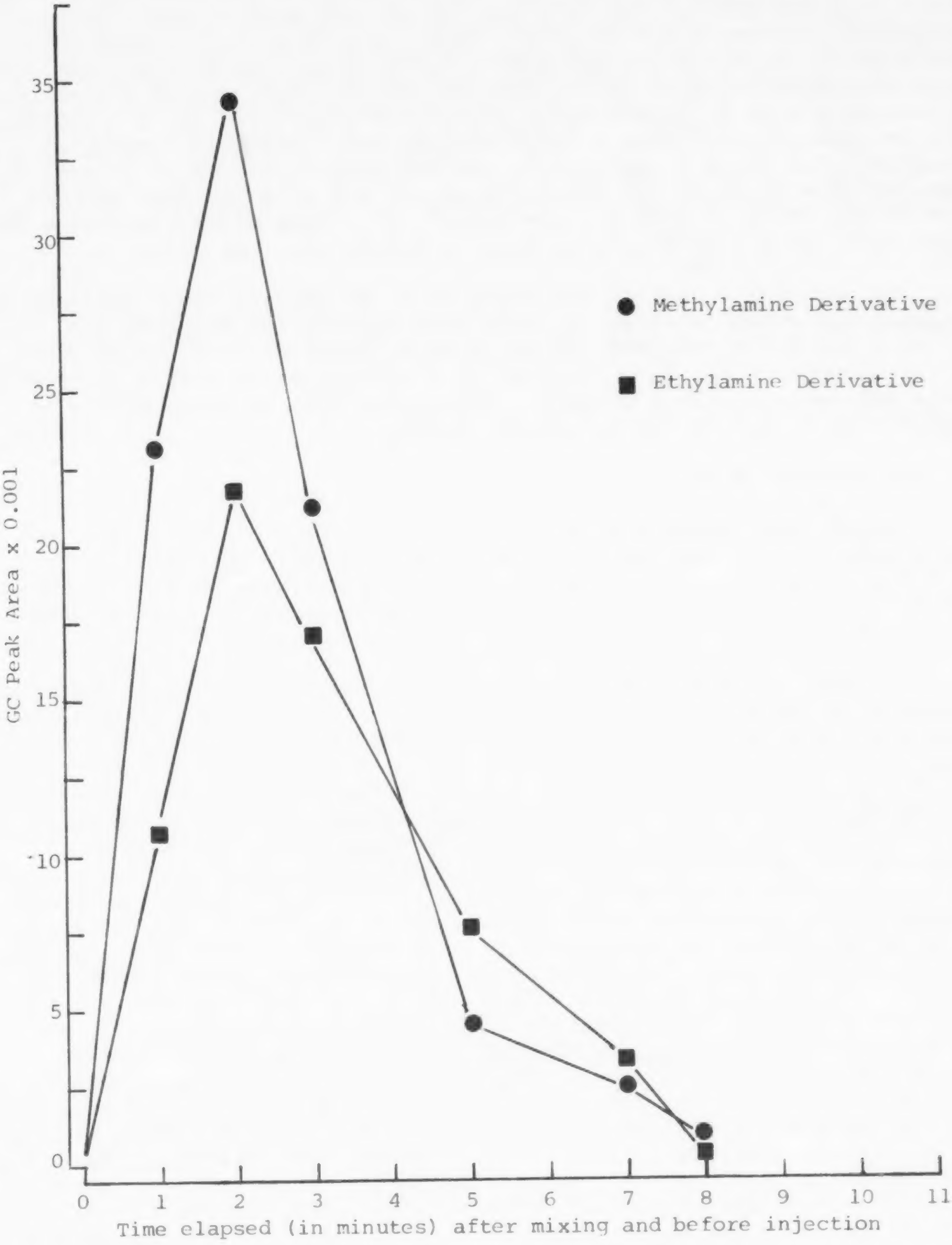


Figure 21. GC peak areas of pentafluorobenzoyl amine derivatives vs time.

The GC-NPD procedure using the Ascarite precolumn has been reevaluated and most of the problems involved with its use have been solved. The inconsistent lifetime of the precolumn remains a problem in the procedure. The syringes can be cleaned by purging several times with the next sample to analyzed. Memory effects in the precolumn and GC column are not a problem as long as a blank is injected into the system after injection of a sample with an amine concentration greater than one ppm. This blank purges out the system for the next sample. The repeatability of the system is also improved if a series of 4-5 injections of a solution containing 1 ppm of each of the amines is made into the system. This must be done each time the instrument has been unused for periods of greater than one hour.

The procedure chosen for the analysis of the organic amines consists of trapping the amines in dilute sulfuric acid solution and analyzing the solution using a GC equipped with an Ascarite precolumn, a 6' x 4 mm glass column packed with 4 percent Carbowax 20 M and 0.8 percent KOH on Carbopax B, and a nitrogen-phosphorus detector. A finalized copy of the procedure is included as an appendix to the interim report.

VALIDATION EXPERIMENTS

Several experiments were carried out to determine the validity of the amine procedure for the analysis of the organic amines. The experiments included checks for GC injection variability, linearity of detector response, sample stability in the absorbing solution, and trapping efficiency of the 0.01 N sulfuric acid solution.

The finalized sampling conditions used to collect the organic amines are listed below, as is a discussion of their selection. A single glass impinger containing 25 mℓ of 0.01 N sulfuric acid is used to collect the organic amines. This single impinger traps 99+ percent of the organic amines at low ppm and ppb amine concentrations. This collection efficiency was determined by bubbling known amounts of organic amines through a series of impingers and analyzing each impinger separately. No advantage was found in using more than one impinger or higher concentrations of sulfuric acid except when the concentration of the amines exceeded 5 ppm. The 0.01 N sulfuric acid concentrations was selected over higher acid concentrations (0.1 and 0.1 N) in order to prevent the neutralization of the ascarite in the precolumn any sooner than necessary. The concentration of the organic amines in exhaust should never approach the 5 ppm concentration; therefore, the single glass impinger containing 0.01 N sulfuric acid should be sufficient to trap the organic amines. Sulfuric acid was chosen over hydrochloric acid as the absorbing acid because of its higher boiling point. Hydrochloric acid is more volatile and could vaporize into the analytical column during analysis. During sampling, the impinger is kept in a 0°C ice bath. The ice bath offers no significant advantage in collection efficiency over room temperature, but does provide a stable sampling temperature during the test. The 0°C temperature also lowers the vapor pressure of the aqueous absorbing solution and thus prevents loss of any significant amount of water from the absorbing solution during sampling. The sample flow rate through the impingers is maintained at 4 liters a minute. This flow rate provides the largest amount of sample flow through the absorbing reagent without loss in absorbing efficiency or the physical loss of any absorbing reagent.

Samples have been found to be stable in the sulfuric acid absorbing solution for months. A two month standard containing 0.1 ppm of mono-, di-, and triemthylamine showed no significant decrease in concentration when compared to a freshly prepared standard. The absorbing solution is also stable over long periods of time with the only worry being contamination from any amines which might be present in the laboratory environment.

To determine the GC injection repeatability for the procedure over a wide range of concentrations, three standards containing 0.01, 0.1, and 1 ppm of mono-, di-, and triethylamine were prepared. Each standard was injected into the GC ten consecutive times. The area of each resulting peak was averaged over the ten runs and a standard deviation was calculated. The results of the injection repeatability experiments are presented in Table 17. Injections of the 0.01 N sulfuric absorbing solution were also made into the GC system. Peaks for monomethylamine and dimethylamine/monoethylamine (the two compounds give one peak in the procedure and are analyzed together as C_2H_7N) were detected in the absorbing solution and gave areas which corresponded to 50 percent of the area for the monomethylamine and diemthylamine in the 0.01 ppm standard and 20 percent of the monoethylamine in the 0.05 ppm standard. The procedure is not as sensitive to the ethylamines as it is to the methylamines; therefore, higher concentrations of the ethylamines (10, 1, 0.1 ppm) were used in the repeatability experiments. For the methylamines the injection repeatability improves with increasing concentration of the methylamines. The standard deviation for the 1 ppm standard containing mono-, di-, and trimethylamine is 5-6 percent, while the deviation for the 0.1 ppm standard is slightly higher at 7-8 percent. The standard deviation for the 0.01 ppm standard is even larger at 12-21 percent. Concentrations at or below 0.01 ppm of the methylamines are difficult to determine due to the poor injection repeatability and the interference from the absorbing solution. The injection repeatability follows no definite trend for the ethylamines. The standard deviations for mono-, di-, and triethylamine remain relatively constant at the three concentrations studied (0.1, 1, and 10): 7-8 percent for monoethylamine, 4-7 percent for dimethylamine, and 7-10 percent for triethylamine. Concentrations below 0.05 ppm of the ethylamines are difficult to determine due to the broadness of the diethylamine and triethylamine peaks and to the interference from the absorbing solution.

To determine the linearity of the nitrogen-phosphorus detector for each of the amines at the concentration ranges of interest, standard solutions containing 0.01, 0.05, 0.1, 0.5, and 1 ppm of mono-, di-, and trimethylamine, and 0.05, 0.1, 1, 5, and 10 ppm of mono-, di-, and trimethylamine were prepared. These were made by weighing out required amounts of each of the organic amine-hydrochloric acid salts and dissolving them in the proper amount of sulfuric acid absorbing solution. Figures 22-27 show plots of the GC peak areas versus the concentration for each of the organic amines on a

TABLE 17. INJECTION REPEATABILITY EXPERIMENTS

Amine	Concentration (ppm)	Average Area	Standard Deviation	Percent Deviation
Monomethylamine	1	8803	533	6.1
	0.1	2004	134	6.7
	0.01	1305	276	21.1
Dimethylamine	1	7081	372	5.3
	0.1	1385	96	6.9
	0.01	1006	117	11.6
Trimethylamine	1	5778	276	4.8
	0.1	1044	87	8.3
	0.01	344	46	14.2
Monoethylamine	10	10,943	977	8.4
	1	8189	626	7.6
	0.1	2748	178	6.5
Diethylamine	10	7025	483	6.9
	1	3460	134	3.9
	0.1	724	32	4.4
Triethylamine	10	10,921	1014	9.3
	1	5446	564	10.4
	0.1	1481	110	7.4

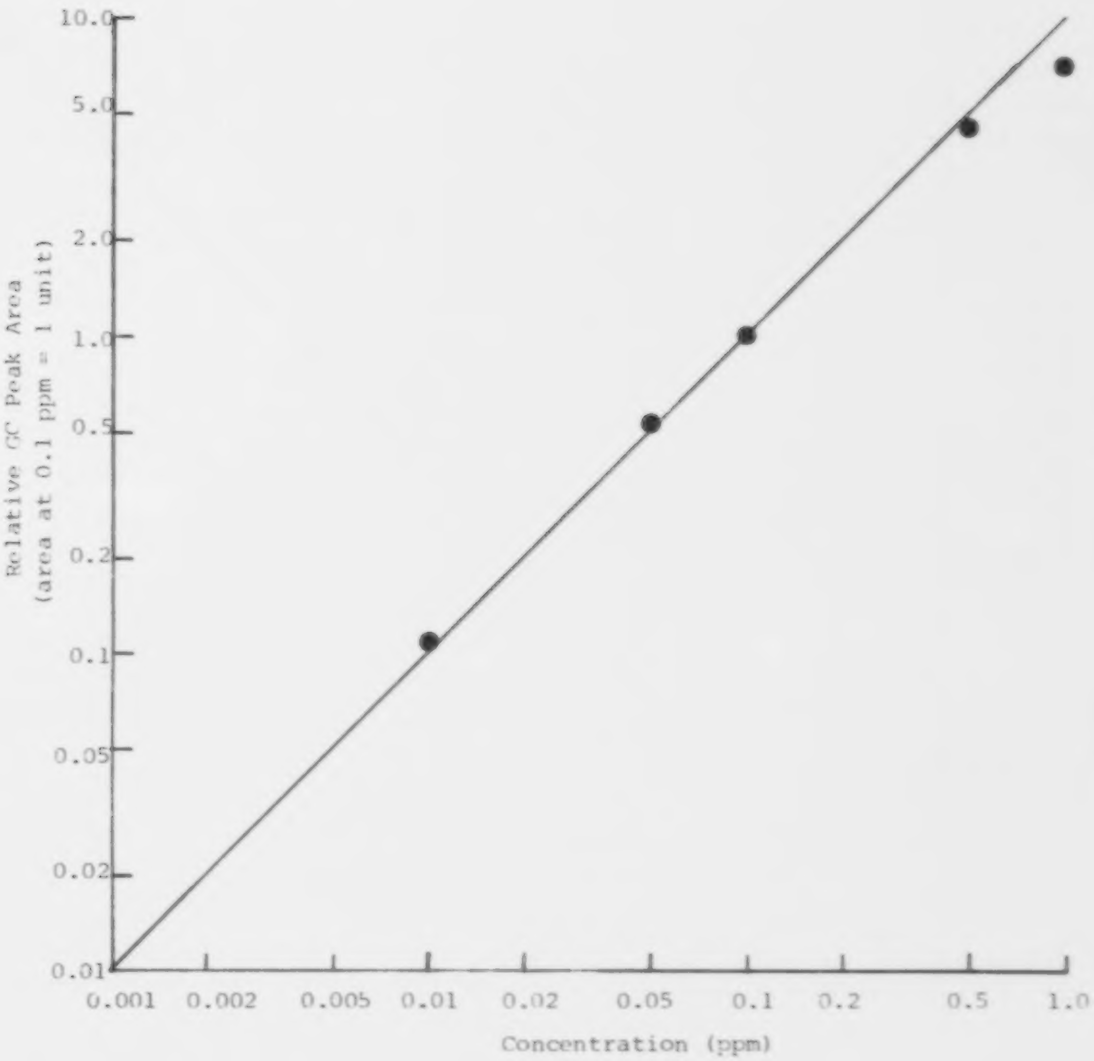


Figure 22. Linearity of monomethylamine GC response (plot on log-log scale).

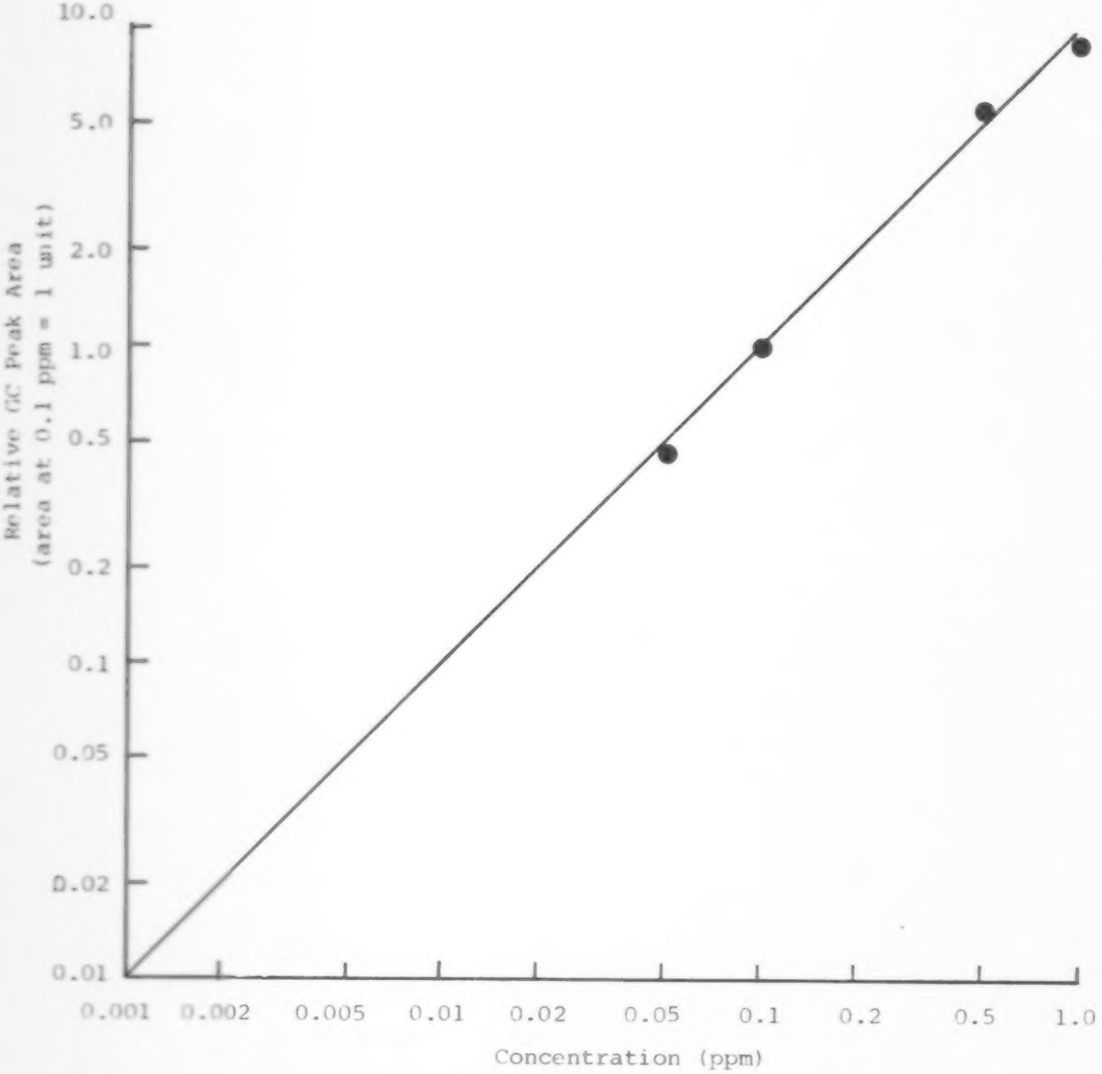


Figure 23. Linearity of dimethylamine GC response (plot on log-log scale).

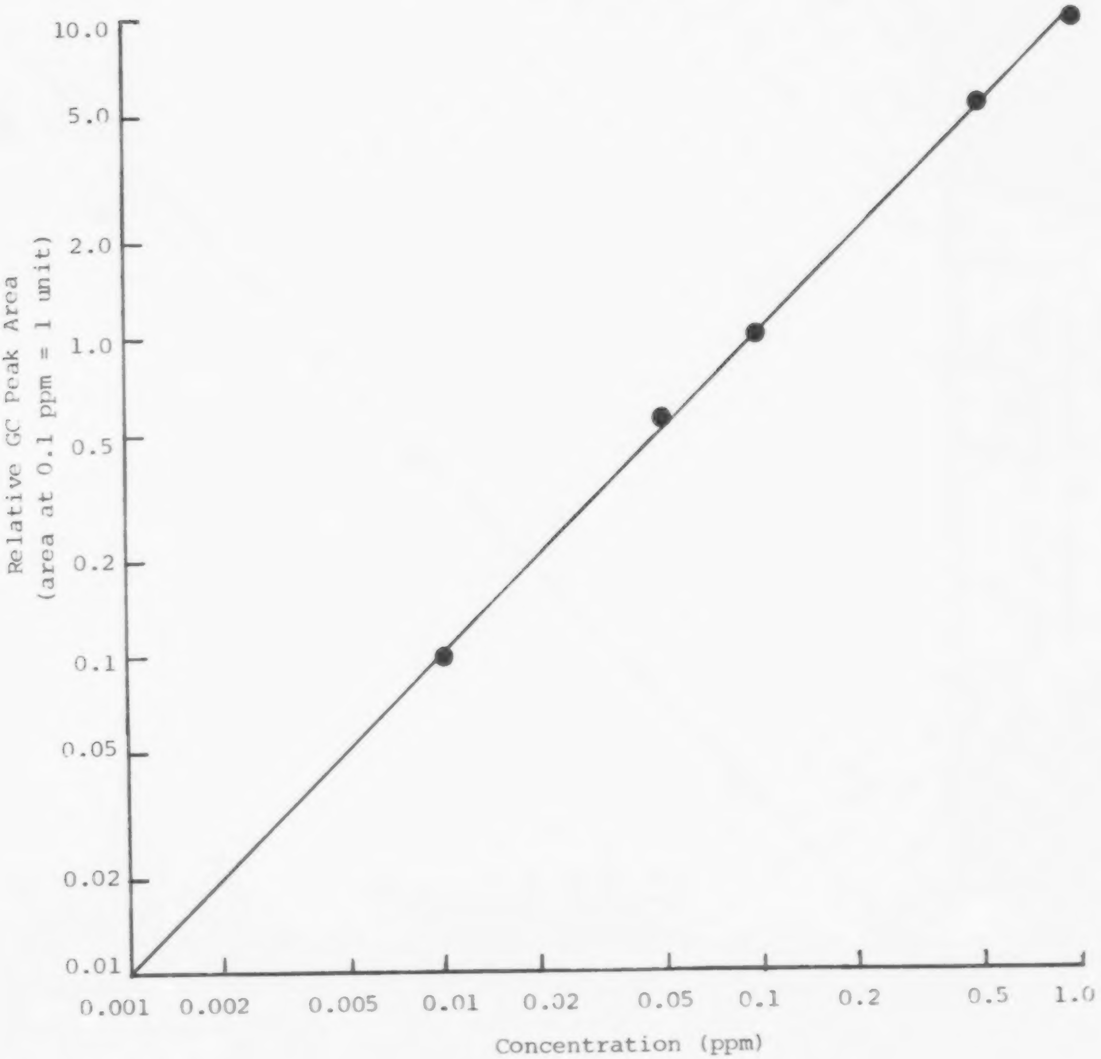


Figure 24. Linearity of trimethylamine GC response (plot on log-log scale).

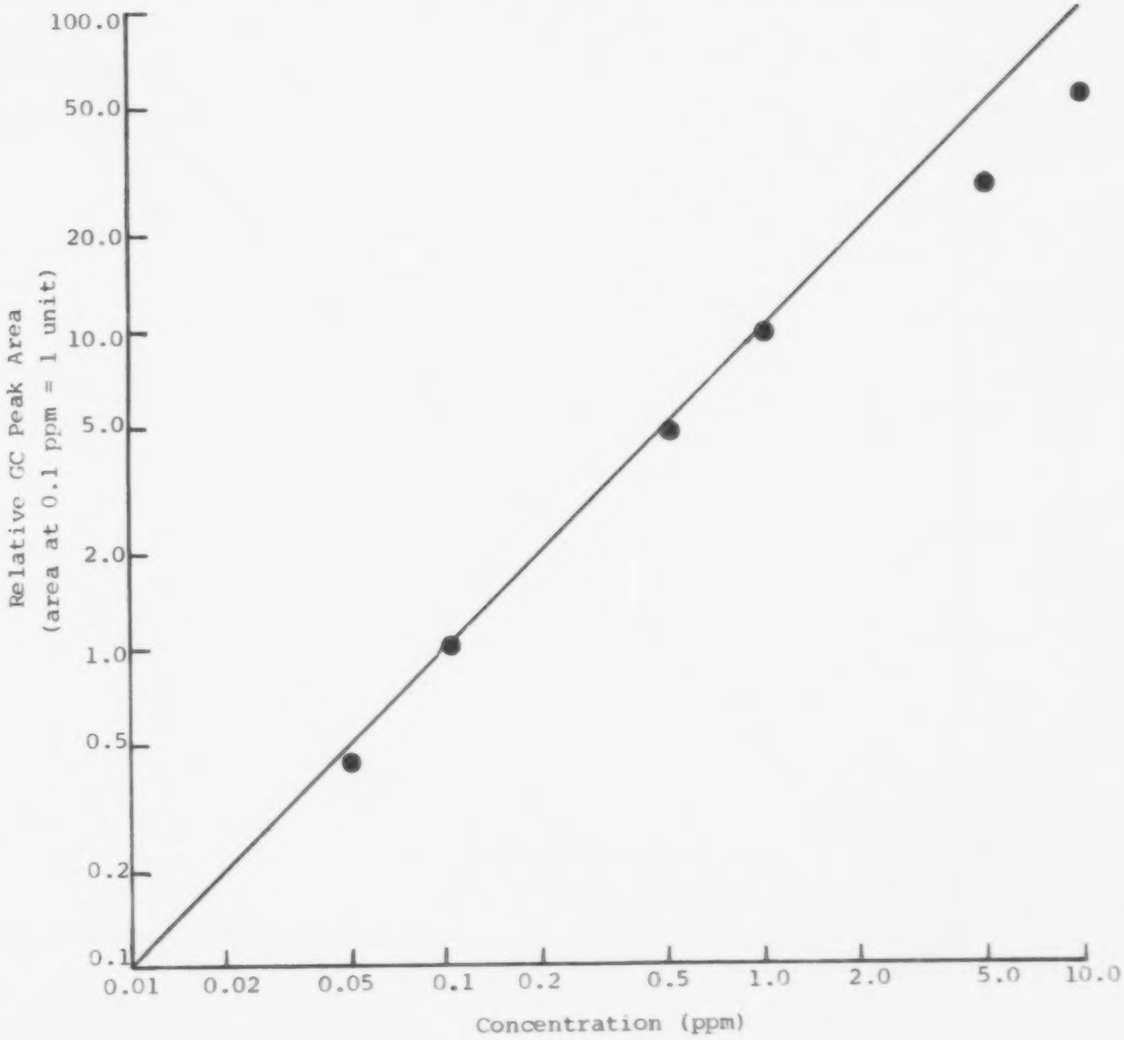


Figure 25. Linearity of monoethylamine GC response (plot on log-log scale).

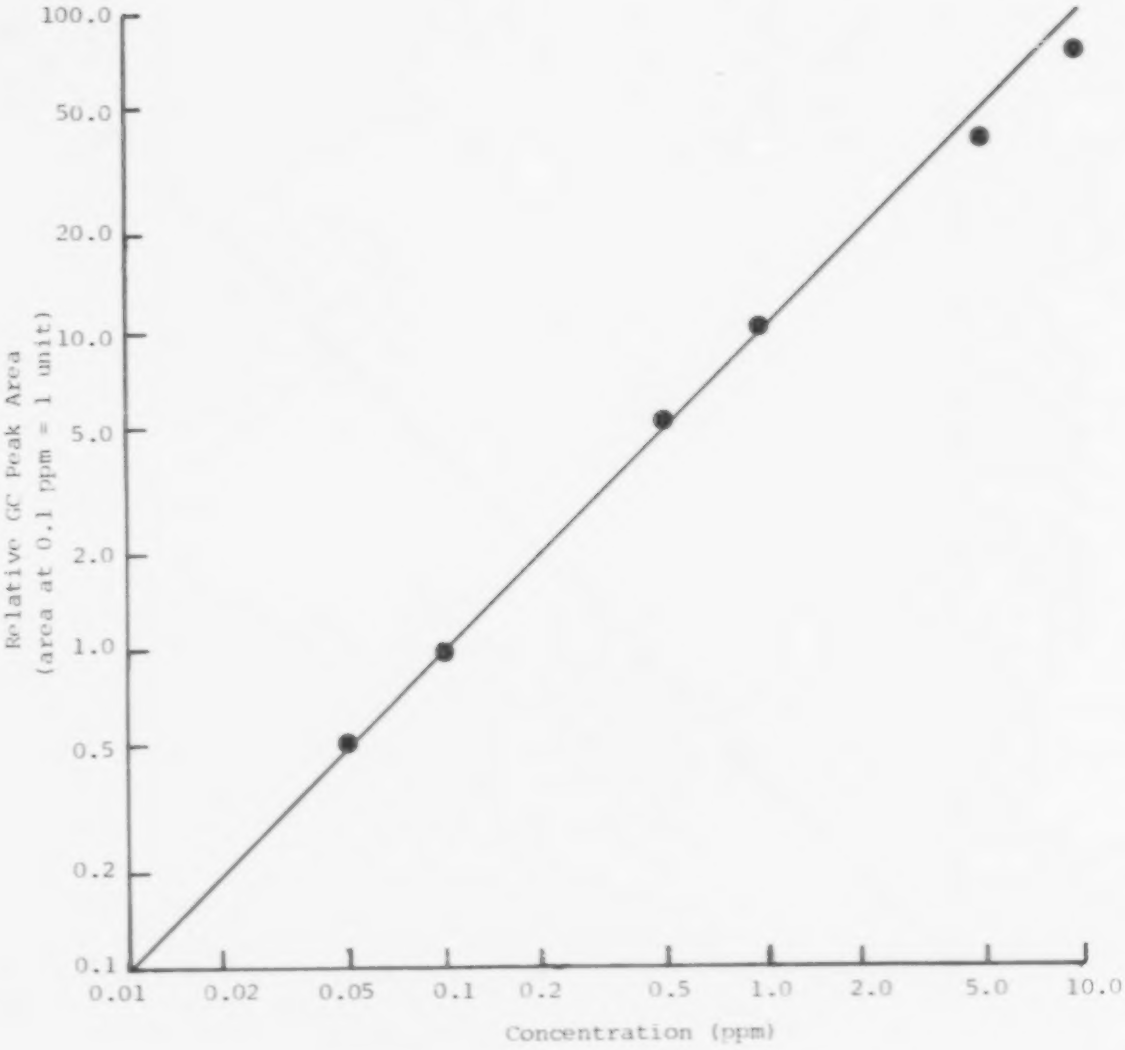


Figure 26. Linearity of diethylamine GC response (plot on log-log scale).

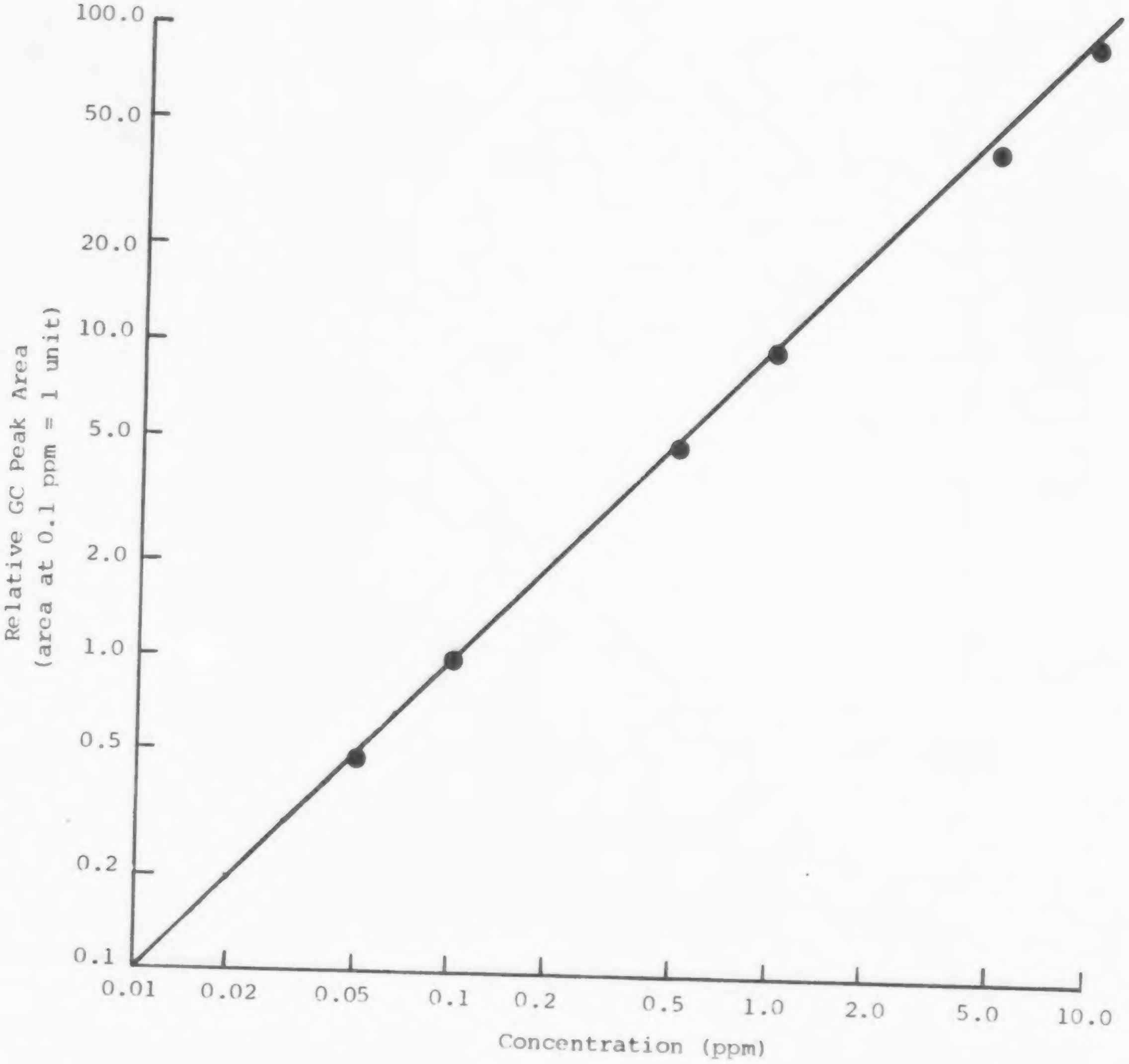


Figure 27. Linearity of triethylamine GC response (plot on log-log scale).

log-log scale. The relative GC areas for monomethyl-, dimethyl- and monoethylamine were corrected for the background peaks found in the absorbing solution. Mono-, di-, and trimethylamine give linear GC responses from 0.01 to 1 ppm and di-, and triethylamine give linear responses in the 0.05 to 10 ppm region. Monoethylamine gives a linear response from 0.05 ppm to 1 ppm, but shows some deviation from linearity in the 1.0 to 10 ppm range.

Ammonia at concentrations between 10-100 ppm in sulfuric acid does not give as large a peak as does a 0.01 ppm solution of monomethylamine, and therefore does not present any major problems as an interference. However, the retention time (0.6 min) is close to that of monomethylamine (0.85 min) and care must be taken not to confuse one peak for the other. Acetonitrile (CH_3CN) had been found in exhaust at concentrations near the 0.1 ppm level. The NPD is sensitive to this compound and gives a peak in the chromatogram at a retention time of 1.8 minutes. This retention time is near that of trimethylamine (2.0 min) and care must be taken not to confuse the two compounds. No other compounds in exhaust have been found to be interferences in the procedure.

QUALIFICATION EXPERIMENTS

Qualification experiments were carried out using a Mercedes 240D vehicle. Hot FTP (23 minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel plus vehicle exhaust experiments. Two aluminum cylinders each containing three amines were used in the experiments. One cylinder contained 174 ppm monomethylamine, 132 dimethylamine, and 107 ppm trimethylamine. The second cylinder contained 408 ppm monomethylamine, 241 ppm dimethylamine, and 123 ppm trimethylamine. The cylinders were named by diluting the amine gas stream 300 fold with zero air, collecting the diluted sample in 0.01 N sulfuric acid and analyzing the sample with GC-NPD. The baseline emission values from the test vehicles were found to be less than 0.005 ppm for all six amines investigated. A test sequence was developed to determine the injection recovery for the three methylamines from the CVS tunnel (18 inch diameter) without exhaust present. Four tests were conducted for the amines at ppm levels ranging from 0.13 to 0.22 ppm. Each test was conducted on a sequence basis with a 10 minute soak with the CVS off between each 23 minute collection interval. The sample lines were heated to 175°F to prevent amine losses in the sample lines. The results of these experiments are presented in Table 18. As expected, the recovery of the methylamine was very low (0.7 - 10.2 percent) for the amine injections. Dimethylamine recovery increased from 4.6 to 27.3 percent after four consecutive injections. Recoveries for trimethylamine were more reasonable with 51.8 to 87.9 percent recovery for four consecutive tests. These results are similar to those obtained in qualification experiments for gasoline-powered vehicles (1).

To determine the percent of amine recovery in the presence of exhaust, a similar set of experiments was carried out. The Mercedes 240D was used to generate exhaust during the 23 minute sampling period. All other parameters were the same as described above and in Table 18, with the exception of adding a non-heated filter in the sample line. This filter was used to

TABLE 18. ORGANIC AMINE RECOVERY FROM THE CVS DILUTION TUNNEL ONLY

Amine Injected	ppm Amine Injected	Nominal Flow Rate, ft^3/min Amine Blend	Nominal Flow Rate, ft^3/min CVS	Run	Calculated ppm amine dilute	Observed ppm	Percent* Recovery
Monomethylamine	174	0.4	320	1	0.22	0.001	0.7
Monomethylamine	174	0.4	320	2	0.22	0.003	1.4
Monomethylamine	174	0.4	320	3	0.22	0.008	3.7
Monomethylamine	174	0.4	320	4	0.22	0.022	10.2
Dimethylamine	132	0.4	320	1	0.17	0.008	4.6
Dimethylamine	132	0.4	320	2	0.17	0.016	9.9
Dimethylamine	132	0.4	320	3	0.17	0.032	19.1
Dimethylamine	132	0.4	320	4	0.17	0.045	27.3
Trimethylamine	107	0.4	320	1	0.13	0.069	51.8
Trimethylamine	107	0.4	320	2	0.13	0.119	89.1
Trimethylamine	107	0.4	320	3	0.13	0.087	66.7
Trimethylamine	107	0.4	320	4	0.13	0.118	87.9

---

* All values are the average of three independent samples.

prevent particulate from contaminating the sampling system. Only trace amounts of amines were recovered in these experiments. The tests were repeated using a heated filter and higher concentrations of the three methylamines. The heated filter and the sample line connecting the dilution tunnel and the heated filter were heated to 375°F. The line connecting the heated filter and the sampling system was maintained at 175°F.

A new amine cylinder (higher in amine concentrations) and lower dilution ratios was used to give expected ppm levels of 0.21 to 0.68 ppm in the dilution tunnel. The results of these experiments are presented in Table 19. The methylamine recoveries ranged from 12.0 to 27.3 percent, dimethylamine recoveries ranged from 18.6 to 44.2 percent and trimethylamine recoveries ranged from 47.6 to 59.5 percent recovery. If a heated filter is used it is possible to detect amines in exhaust at 0.2 ppm and higher levels. At levels lower than 0.2 ppm, losses to the dilution tunnel and to the exhaust may prevent the detection of the amines.

At this time, it is uncertain as to the precise reasons for the losses, but all possible steps have been made to preserve the integrity of the sampling system and the sample handling prior to injection into the gas chromatograph. It is doubtful that any substantial improvement could be made to the system without going to heating the tunnel, etc. The losses of the low molecular weight amines were not unexpected and these experiments confirmed those fears. In summary, methyl- and dimethylamine had low recoveries in the tunnel with and without exhaust present. Trimethylamine recoveries were generally higher and improved with the number of consecutive injections.

RESULTS AND CONCLUSIONS

The concentration of organic amines in dilute exhaust can be determined by collecting the amines in 0.01 N sulfuric acid and analyzing the solution with a GC equipped with an ascarite precolumn and a nitrogen phosphorus detector. The amines are effectively trapped in 25 mℓ of 0.01 N sulfuric acid absorbing solution at a flow rate of 4 ℓ/min. For a twenty-three minute test and a sample flow rate of 4 ℓ/min, the procedure has a minimum detection limit of 2 ppb for each organic amine.

The accuracy of the procedure decreases as the concentration of the amine in the absorbing solution decreases. At a 0.01 ppm concentration of the organic amines in the absorbing solution, the present standard deviation for the GC is 12-21 percent. The absorbing solution itself gives peaks equal to 0.005 ppm monomethylamine and dimethylamine/ethylamine. At the 0.01 ppm level or lower it is difficult or impossible to determine the concentration of amines. This concentration is equivalent to 2 ppb of the amines in dilute exhaust (23 minute test, sampling at 4 ℓ/min.)

Acetonitrile and ammonia have been found in exhaust samples and give peaks in the chromatograms. Ammonia at concentrations of 10-100 ppm gives a peak approximately the size of a 0.01 ppm methylamine peak. The separation of the ammonia and the methylamine peak is 0.25 minutes, but the two can easily be distinguished if care is taken. Acetonitrile has a retention time

TABLE 19. ORGANIC AMINE RECOVERY FROM THE CVS DILUTION TUNNEL WITH EXHAUST

Amine Injected	ppm Amine Injected	Nominal Flow Rate, ft^3/min		Run	Calculated ppm amine dilute	Observed ppm	Percent* Recovery
		Amine Blend	CVS				
Monomethylamine	408	0.5	300	1	0.68	0.092	12.0
Monomethylamine	408	0.5	300	2	0.68	0.156	22.9
Monomethylamine	408	0.5	300	3	0.68	0.186	27.3
Dimethylamine	241	0.5	300	1	0.40	0.074	18.6
Dimethylamine	241	0.5	300	2	0.40	0.139	34.7
Dimethylamine	241	0.5	300	3	0.40	0.177	44.2
Trimethylamine	123	0.5	300	1	0.21	0.098	47.6
Trimethylamine	123	0.5	300	2	0.21	0.112	54.9
Trimethylamine	123	0.5	300	3	0.21	0.122	59.5

---

* All values are the average of three independent samples

that differs from trimethylamine by only 0.2 minutes, but the two can also be easily distinguished.

The amines are notorious for sticking to metal sites. The qualification experiments represent another example of this problem. The amines had low percent recoveries from the CVS dilution tunnel with and without exhaust present. The percent recovery increased directly as the number of injections into the tunnel increased. This phenomenon is probably due to the gradual coating of the tunnel with the amines, thus neutralizing the number of metal sites in the tunnel. It is possible that if the amines are present in concentrations of less than 0.2 ppm, the percent recovery may be very low or essentially zero.

The organic amine procedure should provide a relatively accurate method for determining the concentration of the organic amines exiting the CVS tunnel; however, amine losses in the CVS tunnel must be taken into account when reporting these concentrations.

SECTION 6

SULFUR DIOXIDE PROCEDURE

LITERATURE SEARCH

At room temperature and atmospheric pressure sulfur dioxide is a highly irritating, nonflammable, and colorless gas. The gas is readily detectable at concentrations of 3-5 ppm by the human sense of smell. Physical properties of sulfur dioxide, SO_2 (sulfurous acid anhydride) include a freezing point of -75.5°C (1 atm), a boiling point of -10.0°C (1 atm), and a molecular weight of 64.063 (12).

The bulk of published literature regarding the analysis of sulfur dioxide has dealt with ambient air sampling. With the development of instrumental methods of analysis, the ability to measure sulfur dioxide in stationary and mobile source exhausts now exists. The following review of references reveals a wide variety of analytical techniques used in the measurment of sulfur dioxide concentrations.

A frequently used method for the analysis of sulfur dioxide is a colorimetric method. The most commonly employed colorimetric technique is the West-Gaeke method (31-35). This method has been collaboratively tested, with the lowest concentration range studied being well above the levels most frequently found in rural and global background air (36).

A modified version of the West-Gaeke method involves the collection of sulfur dioxide in 0.1 M sodium tetrachloromercurate(II) (TCM). Sulfur dioxide reacts with the TCM to form a dichlorosulfiromercurate complex (DCSM). In this modified version, the DCSM resists oxidation by oxygen in the air and oxygen dissolved in the absorbing solution. Ethylenediamine tetracetic acid disodium salt (EDTA) is added to the TCM absorbing solution to complex any heavy metals that could oxidize sulfur dioxide before the DCSM is formed (37,38), and sulfamic acid is added to the absorbing solution to destroy any interfering nitrite ion which might be present (39).

The colorimetric determination of sulfur dioxide is based upon the measurement of the red-violet color produced by the reaction of DCSM with hydrochloric acid, pararosaniline and formaldehyde. The effect of the pararosaniline dye purity on the colorimetric procedure has been reported by several researchers (40,41). Since the dye purity does effect the results of the colorimetric procedure, various techniques for the purification of commercial grade pararosaniline have been published (32,34,42), and pararosaniline purified especially for the colorimetric analysis of sulfur dioxide is commercially available (42).

A major potential source of error associated with the West-Gaeke colorimetric method for measuring sulfur dioxide is the widely differing collection efficiency reported for Greenburg-Smith and midget impingers at low sulfur dioxide concentrations (43). Urone, et al, investigated the collection efficiency of the TCM solution by the use of microgram quantities of sulfur dioxide tagged with ^{35}S (44). In this investigation, it was found that a series of bubblers cannot be used to determine absorber collection efficiency. Bostrom obsered a 99 percent collection efficiency for a concentration range 100-1000 ppb sulfur dioxide in a TCM solution (45).

Work has been conducted in the development of other colorimetric methods for the analysis of sulfur dioxide. Attari developed a procedure whereby sulfur dioxide is absorbed into a solution of ferric ammonium chloride, perchloric acid, and phenanthroline dye (46). A color complex with an absorbance of 510 mm was formed, and although the color developed within 10 minutes, it tended to fade with time. Hydrogen sulfide was found to be an interference in the procedure.

Kawai used the reaction of barium chloranilate with sulfate as an indirect measurement of sulfur dioxide (47). Sulfur dioxide was absorbed in a solution containing hydrogen peroxide and barium chloranilate. Barium chloranilate reacts with the sulfate ion producing a red-violet chloranilic acid ion. Although this method may be satisfactory for flue gas analysis, it lacks the sensitivity required for ambient air analyses.

Conductivity methods have been used for continuously monitoring sulfur dioxide in air (48). The conductivity of a dilute sulfuric acid-hydrogen peroxide reagent changes due to the absorption of pollutants. This change in conductivity is assumed to result primarily from sulfur dioxide absorbed from the sampled air and oxidized to sulfuric acid. In many cases, sulfur dioxide is the major pollutant present; however, if other pollutants are present, their collection efficiency and solubility may be significantly different than for sulfur dioxide. Several field comparisons of conductivity with other sulfur dioxide procedures indicate a fair agreement (49-54). Hydrochloric acid gas, ammonia, and chlorine substantially increase conductivity. Shikiya and McPhee found two- to fourfold differences between different conductivity analyzers and between conductivity and colorimetric analyzers (51). Although the conductivity procedure may be acceptable for point sources of sulfur dioxide in isolated areas, its high potential for positive and negative interferences limits its application.

Iodometric methods were among the first adapted for air pollution analysis from the industrial hygiene literature. With this method, the sulfur dioxide is collected in an impinger containing standard NaOH absorbing solution. The absorbing solution is acidified and the liberated sulfurous acid is titrated with a standard iodine solution (52). Another method employs a standard iodine-potassium absorbing solution (53). Iodometric methods of analysis for sulfur dioxide generally suffer from a lack of sensitivity and interferences from hydrogen sulfide.

Adsorption sampling methods have also been developed for the measurement of sulfur dioxide (55). Sulfur dioxide is absorbed on silica gel, desorbed, and reduced to hydrogen sulfide at 700-900°C over a platinum catalyst. The hydrogen sulfide is then absorbed in a 2 percent ammonium molybdate solution and determined colorimetrically. Although this technique is relatively specific for sulfur dioxide, the final colorimetric determination by the molybdenum complex does not utilize the most sensitive method available.

In addition to the aforementioned techniques, sulfur dioxide has been measured by filtration (56-60) and static collectors (61-67). Air samples are passed through potassium bicarbonate impregnated filters and analyzed for sulfate. The collection efficiency of these filters is dependent upon humidity, temperature, and the atmospheric concentration of sulfur dioxide. The lead peroxide candle static collector was developed by Wilson and McConnell as an inexpensive method for measuring relative "sulfation" of the atmosphere (61). The sulfur dioxide collection efficiency is dependent upon temperature, relative humidity, wind speed, atmospheric concentration of sulfur dioxide, and the length of exposure period (62). Ikeda determined ambient sulfur dioxide levels by collecting samples on active carbon filters, washing the filters with distilled water, and titrating with barium chloranilate (67).

With the advent of modern instrumental methods of analysis, specifically gas and ion chromatography, a substantial amount of data has been published. Most trace gas analysis for sulfur dioxide has been conducted using gas chromatographs with flame photometric detectors (FPD) (68-77). The FPD is highly selective for sulfur compounds and has low minimum detection limits. Analysis for sulfur dioxide is generally performed using all Teflon or glass systems. Sulfur dioxide will react with active sites in the gas chromatograph system, making the use of inert materials essential for trace quantitative analysis. Gas chromatographs with FPD and linearizing circuitry provide a wide dynamic range for ambient and source sulfur dioxide levels. In some instances, the collection technique precludes the use of GC-FPD techniques; i.e., bag sampling from dilute automotive exhaust or source sampling. The use of gas chromatography would be a prime candidate if the sample integrity could be assured in the sample acquisition and subsequent analysis.

A more recent development in methods of analysis for sulfur dioxide involves the use of ion chromatography (78). This technique involves collection in a hydrogen peroxide absorbing reagent and measurement of the resulting sulfate ion using ion chromatography. Ion chromatography is a specialized area of liquid chromatography which will separate and quantify the individual cations or anions. This technique has been applied to the measurement of sulfur dioxide in ambient air.

Other instruments are commercially available that are reported to measure sulfur dioxide in ambient or dilute automotive exhaust. Such instruments include continuous detection by pulsed fluorescent UV and second derivative UV analyzers. A pulsed fluorescent UV analyzer for sulfur dioxide was found to give recoveries on the order of 115-125 percent, indicating that a positive interference is present (79). The second derivative

UV sulfur dioxide analyzer has inherent problems when being used on continuous samples. The mirrors are located in the actual cell and become coated with various exhaust components even after filtration of the sample. The mirrors will become etched and need resurfacing if the unit is used in the presence of sulfur dioxide, sulfate ion, or other corrosive exhaust components. The inherent noise level, along with the consistent mirror problem, preclude the use of second derivative UV analyzer for measuring sulfur dioxide on a continuous basis.

A variation of the GC method for measuring sulfur dioxide is the use of a continuous analyzer using an FPD detector. Although this approach is good in theory, it has several problems associated with the performance of the FPD detector. These units were originally designed to monitor sulfur dioxide levels in the ambient air and adaption to automotive exhaust was not staightforward. Air samples had essentially the same oxygen and nitrogen levels all of the time; however, dilute exhaust samples have variable carbon dioxide, oxygen and nitrogen concentrations. The species have been found to cause quenching effects on a FPD detector. With the constantly changing carbon dioxide, oxygen, and nitrogen it would be impossible to correct for any quenching effect. The use of a continuous FPD analyzer for measuring sulfur dioxide in automotive exhaust would not be acceptable unless the quenching effects could be eliminated.

PROCEDURAL DEVELOPMENT

From the results of the literature search it was determined that the analysis of sulfur dioxide should be conducted by the use of ion chromatography. An ion chromatograph built at Southwest Research Institute was dedicated for this purpose. This instrument utilizes a modified Swagelok reducing union for a conductivity cell, a Hall conductivity detector, a Milton Roy mini-pump, a Soltec multivoltage recorder, a Glenco Scientific pulse dampener, and polyethylene cubitainers from Cole Parmer Instrument Company for the analysis of sulfur dioxide. A minimal amount of procedural development work was necessary for this procedure; however, several instrument and sampling parameters did have to be determined. The selection of these parameters are discussed in detail in the Validation Experiments section.

In order to analyze automotive exhaust for sulfur dioxide, a trap or an absorbing reagent must be used to concentrate the sulfur dioxide. A method which has been previously used at Southwest Research Institute for collecting and concentrating sulfur dioxide was selected and validated for use in this project. This method consists of bubbling dilute exhaust through a dilute aqueous hydrogen peroxide solution. The hydrogen peroxide reacts with the sulfur dioxide to give sulfate ion which remains in the absorbing solution.

The parameters selected for the analysis of sulfur dioxide are listed below. The sulfur dioxide from the exhaust is bubbled through two impingers (maintained at ice bath temperatures) in series with each impinger containing 25 mℓ of a 3 percent hydrogen peroxide solution. The exhaust flows through the impingers at a rate of 4 ℓ/min. Two impingers together trap 99 percent of the sulfur dioxide present in exhaust. A heated glass fiber filter is installed in the sampling line prior to the bubblers to remove particulate which could contaminate the separator column during analysis. A portion of the absorbing solution is loaded into the sample loop and injected into the ion chromatograph. For analysis the ion chromatograph utilized three columns and an eluent composed of 0.003 M $NaHCO_3$ plus 0.0024 M Na_2CO_3. The eluent flows at 30 percent of full pump capacity through a 3 x 150 mm precolumn (this column helps prevent contamination of the separator column), a 3 x 500 mm separator column and a 6 x 250 mm suppressor column packed with AG 50W-X16 anion suppressor resin (this neutralizes the ionic effect of the eluent while increasing that of the sample ion). A finalized copy of the procedure is included as an appendix to the interim report.

VALIDATION EXPERIMENTS

Sulfur dioxide validation experiments were performed to verify the sampling and instrument parameters. These experiments involved the determination of sampling flowrate, sampling temperature, kind and concentration of absorbant and the number of bubblers required to collect 100 percent of the sulfur dioxide. The variables associated with the ion chromatograph that were determined included type and concentration of eluent, injection loop size, flowrate, injection variability, and linearity of response. In addition to determining sampling and instrument parameters, validation experiments were performed to verify certain portions of the procedure for sulfur dioxide analysis. Tests for interferences, sample stability, and standard stability were among those conducted. Also, the method of washing glassware was studied.

A number of possible interferences were tested by bubbling the suspected interfering gas at 4 ℓ/min through three impingers in series. Each impinger contained 25 mℓ of 3 percent hydrogen peroxide and was maintained at ice bath temperatures (0-5°C). The tests lasted approximately twenty minutes each. The results are shown in Table 20. In the zero air, zero nitrogen, 3 percent CO_2 and 100 ppmc HC tests, no detectable amount (less than 0.01 ppm SO_2) was found. A positive interference of 0.01 ppm SO_2, was found in the 100 ppm NO_x test. The greatest interference, 0.02 ppm SO_2, was found in the 100 ppm CO test. Another source of interference was caused by the sulfuric acid-chromic acid bath in which the impingers were washed. The sulfate ion from the sulfuric acid could not be sufficiently rinsed from the impingers, even with repeated deionized water rinses. For this reason, a 1:1 (v:v) nitric acid and water solution was used to wash the impingers used in the sulfur dioxide procedure. The sulfate present in the hydrogen peroxide absorbing solution also causes a positive interference. This interference could be corrected for by subtracting the sulfate peak area of the absorbant from the sulfate peak area of exhaust or background samples.

Another validation experiment for the ion chromatographic method of sulfur dioxide analysis involved determining the stability of samples and standards over a period of time. The sulfuric acid standards made up in filtered deionized water remained stable for at least fourteen weeks. Sulfate standards made up from stock solutions prepared on 11/30/77 and 3/13/78 were analyzed on 3/13/78 and the peak areas were compared. The results, shown in Table 21 indicate that the fourteen week old standards repeated within 10 percent of

TABLE 20. INTERFERENCES TO SO_2 ANALYSIS

Suspended Interference	Concentration SO_2 (ppm SO_2)			Total SO_2(ppm)
	Bubbler 1	2	3	
Zero Air	0.00	0.00	0.00	0.00
Zero N_2	0.00	0.00	0.00	0.00
3% CO_2-run 1	0.00	0.00	0.00	0.00
3% CO_2-run 2	0.00	0.00	0.00	0.00
100 ppmc HC	0.00	0.00	0.00	0.00
100 ppm NO_x	0.01	0.00	0.00	0.01
100 ppm CO	0.01	0.01	0.00	0.02

TABLE 21. SULFATE STANDARD STABILITY

Standard Concentration $\left(\frac{\mu g\ SO_4^{-2}}{m\ell}\right)$	Standard Preparation	Attenuation	Height (in)	Amplitude	% Difference
0.96	(11/30/77)	3	4.73	125,844	0.6
0.96	(03/13/78)	3	4.77	125,080	
4.80	(11/30/77)	10	7.72	148,259	0.6
4.80	(03/13/78)	10	7.62	147,300	
9.60	(11/30/77)	30	5.41	130,852	0.1
9.60	(03/13/78)	30	5.45	131,036	
38.40	(11/30/77)	100	7.93	149,864	0.8
38.40	(03/13/78)	100	7.81	148,668	
96.00	(11/30/77)	300	6.09	135,666	0.0
96.00	(03/13/78)	300	6.08	135,638	

the freshly prepared standards. A study was also conducted with a variety of samples of different ages to determine sulfate longevity in the 3 percent hydrogen peroxide absorbant. One week after collection and initial analysis, a sample obtained from an SO_2 exhaust recovery experiment remained at 0.13 ppm SO_2. A two week old 0.06 ppm SO_2 baseline sample produced similar results. There was no change observed in the sulfur dioxide level. A ten week old collection efficiency sample, however, did very from its initial concentration of 0.13 ppm by decreasing 7.9 percent to 0.12 ppm SO_2. This is greater than the injection repeatability of 1.2 percent, however, within the minimum detection limit of 0.01 ppm SO_2. The samples appear to be stable at least two weeks but less than ten weeks, the break-off point probably lying between four and six weeks.

The second portion of validation testing included the determination of SO_2 sampling parameters. Nominal concentrations of 5 and 12 ppm SO_2 were collected for 20 minutes in three bubblers, each containing 25 mℓ of 3 percent hydrogen peroxide. The results of these tests are shown in Table 22.

TABLE 22. SO_2 COLLECTION EFFICIENCY AS A FUNCTION OF FLOWRATE AND TEMPERATURE

Test	Flow-rate (ℓ/min)	Temp, (°F)	SO_2 Concentration (ppm) and (%) in bubbler			Bubbler 1+2+3(ppm)	% SO_2 trapped in bubblers 1 and 2
			1	2	3		
				Nominal 5 ppm SO_2			
1	4	72	4.31(95.3)	0.16(3.4)	0.06(1.3)	4.52	98.7
2	4	32	6.73(96.7)	0.17(2.4)	0.06(0.1)	6.96	99.1
3	2	32	6.48(94.6)	0.21(3.1)	0.16(2.3)	6.85	97.7
4	2	75	6.71(98.8)	0.12(1.8)	0.09(1.4)	6.93	98.6
				Nominal 12 ppm SO_2			
5	4	32	22.4(92.5)	1.25(5.2)	0.54(2.2)	24.2	97.7
6	4	32	24.8(99.1)	0.13(0.5)	0.09(0.4)	25.0	99.6
7	4	32	28.5(99.0)	0.22(0.8)	0.07(0.2)	28.8	99.8
8	4	32	29.3(97.8)	0.35(1.2)	0.30(4.0)	29.9	99.0
9	4	32	30.0(98.5)	0.24(0.8)	0.21(0.7)	30.4	99.3
10	4	32	21.2(97.9)	0.20(0.9)	0.25(1.2)	21.7	98.8
11	4	32	29.9(98.5)	0.23(0.8)	0.23(0.8)	30.4	99.3
12	4	32	28.9(98.5)	0.32(1.1)	0.12(0.4)	29.3	99.6

The largest quantity of sulfur dioxide was retained at a flowrate of 4 ℓ/min at ice bath temperature. Under these conditions, 99.1 percent SO_2 was collected in the first two bubblers. It is also desirable to prevent small particulate debris in the exhaust from entering the samples and, thus, the columns of the ion chromatograph. If this form of contamination is allowed to collect in the columns the liquid flow becomes hampered causing increased backpressure. A glass fiber filter in the sampling line is used to remove a large portion of this debris from the exhaust.

The third portion of validation testing involved the determination of instrument parameters; eluent concentration and flowrate, columns, sample loop size, linearity of response and injection variability. Choice of eluent concentration and flowrate will depend on the columns chosen and the species present in the samples. Exhaust samples contain a variety of amines, fluoride, chloride, nitrite, phosphate, nitrate and sulfate. Nitrate elutes just prior to sulfate necessitating the use of an efficient separator column. A 3 x 500 mm glass column packed with patented resin is the separator column chosen for sulfate analysis. The suppressor column is a 6 x 250 mm glass column with AG 50W-X16 resin. A 0.003 M $NaHCO_3$ and 0.0024 M Na_2CO_3 eluent solution flowing at 30 percent of pump capacity gives good baseline resolution when a 500 μℓ sample loop is used. Another instrument factor which needed to be determined was the injection variability.

The ion chromatograph has an injection repeatability of 1.1 or 1.2 percent as shown in Table 23. This is represented by C_v (coefficient of variation) which is the standard deviation divided by the mean and multiplied by 100. The mean or average is represented by $\bar{x}$ and standard deviation by S_x. For these calculations peak heights instead of peak areas were used since the heights repeated much better and with greater precision than the areas.

Two different standards were analyzed: $0.5 \frac{\mu g\ SO_4^{-2}}{m\ell}$ and $4.0 \frac{\mu g\ SO_4^{-2}}{m\ell}$

The final instrument parameter determined was the linearity of response of sulfate standards at different attenuations. The sulfate standards, made up from sulfuric acid and filtered deionized water, maintained linearity at each attenuation but the slopes became steeper as the sensitivity decreased. Table 24 shows heights corresponding to each standard used and Figure 28 shows the graphical representation of the data. At the 1 x 10 scale setting, the relative slope was 1.7, at the 1 x 30 setting it was 2.5 and at the 1 x 100 setting the slope was 2.6. It was not necessary to carry the curve any further, since no samples have been obtained that fall in the higher concentration range. However, it was found that lineatity was maintained at concentrations from 40 to $100 \frac{\mu g\ SO_4^{-2}}{m\ell}$.

QUALIFICATION EXPERIMENTS

Qualification experiments were carried out to determine the percentage of sulfur dioxide that could be recovered at the sampling point when known amounts of sulfur dioxide were injected into the dilution tunnel at the point where exhaust enters the tunnel. A Mercedes 240D vehicle was used as a source of exhaust. Hot FTP (23-minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel plus vehicle experiments. Aluminum cylinders containing 887 ppm and 9098 ppm sulfur dioxide in balance air were used to inject sulfur dioxide into the CVS dilution tunnel. The flow of sulfur dioxide into the tunnel was regu-

TABLE 23. INJECTION REPEATABILITY FOR ION CHROMATOGRAPH

Sample	Concentration $\left(\frac{\mu g\ SO_4^{-2}}{m\ell}\right)$	Attenuation	Height (in)
1	3.84	1 × 10	5.37
2	3.84	1 × 10	5.43
3	3.84	1 × 10	5.51
4	3.84	1 × 10	5.45
5	3.84	1 × 10	5.50
6	3.84	1 × 10	5.53
			$\bar{x}$ 5.46 in
			S_x 0.06 in
			C_v 1.1%
7	0.48	1 × 10	0.81
8	0.48	1 × 10	0.80
9	0.48	1 × 10	0.79
10	0.48	1 × 10	0.81
11	0.48	1 × 10	0.80
12	0.48	1 × 10	0.81
			$\bar{x}$ 0.80 in
			S_x 0.01 in
			C_v 1.2%

TABLE 24. CALIBRATION CURVE FOR SULFUR DIOXIDE

Standard Concentration $\left(\frac{\mu g\ SO_4^{-2}}{m\ell}\right)$	Attenuation	Height (in)	Heights Corrected to 1 × 10 scale (in)
0.48	1 × 10	0.85	
0.96	1 × 10	1.87	
1.48	1 × 10	2.38	
1.92	1 × 10	3.23	
2.88	1 × 10	4.89	
3.84	1 × 10	6.62	
4.80	1 × 10	8.16	
4.80	1 × 30	2.60	7.80
7.68	1 × 30	4.77	14.31
9.60	1 × 30	6.49	19.47
19.20	1 × 100	3.37	33.70
28.80	1 × 100	6.15	61.50
38.40	1 × 100	8.32	83.20

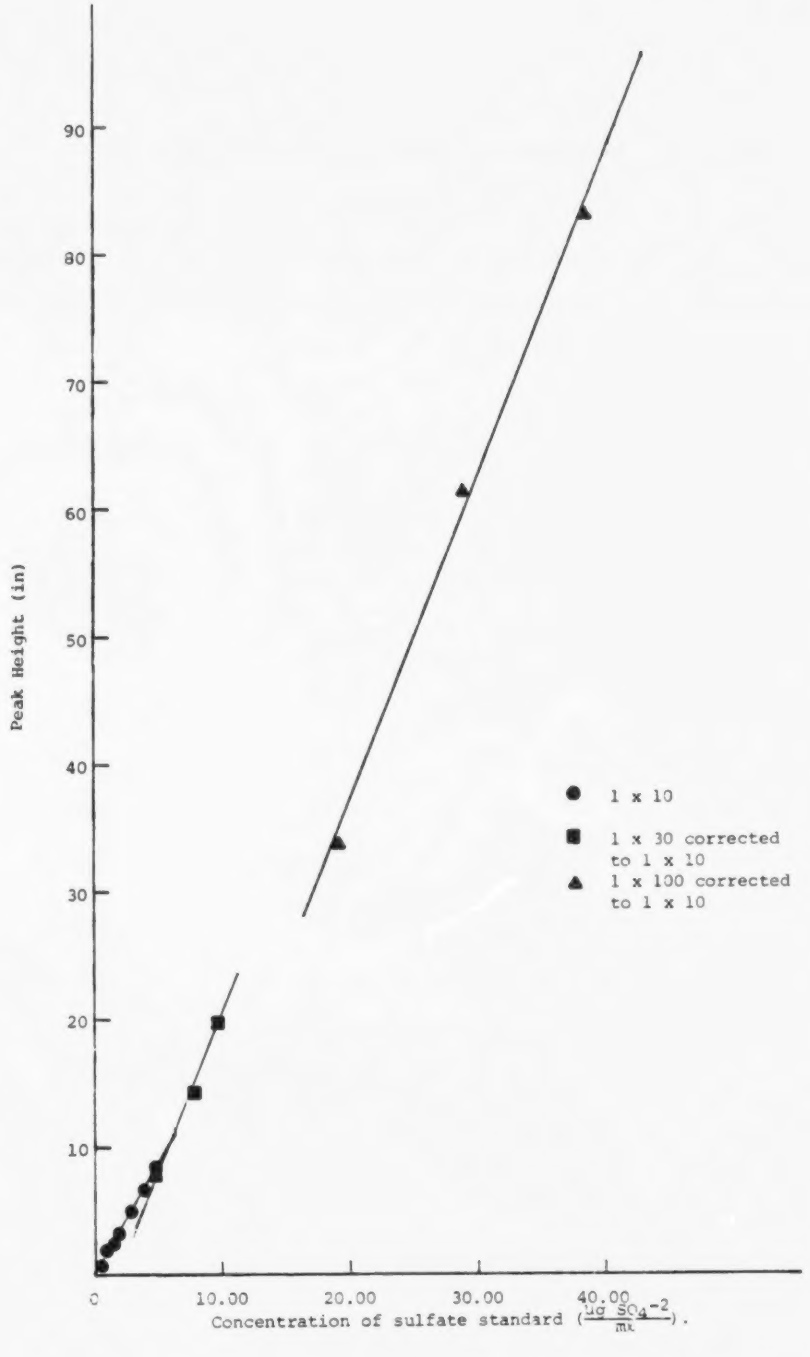


Figure 28. SO_2 calibration curve.

lated to give concentrations of 1 (CVS-tunnel only) to 11 ppm (CVS-tunnel and vehicle exhaust). Injections of sulfur dioxide into the tunnel without exhaust gave recoveries that ranged from 80 to 108 percent with an average of 98 ± 8 percent (Table 25).

The recovery of sulfur dioxide in the presence of vehicle exhaust ranged from 73 to 117 percent with an average of 97 ± 16 percent (Table 26). The sulfur dioxide recoveries were corrected for background levels and for vehicle baseline emissions. Background levels ranged from 0.15 to 0.19 ppm while the vehicle baseline emission levels averaged 7.73 ppm. The recoveries from the tunnel in the presence of vehicle exhaust were carried out using a heated filter and heated sample lines. The filter was used to prevent particulate from contaminating the sampling system. The filter and sample lines were heated to prevent sulfur dioxide from being retained on the removed particulate. The recovery experiments indicate that sulfur dioxide can be quantitatively recovered from the dilution tunnel.

RESULTS AND DISCUSSION

The ion chromatographic method of sulfur dioxide analysis is a simple, sensitive and relatively rapid procedure with a minimal number of interferences. Zero air, nitrogen, 3 percent CO_2 and 100 ppmc HC did not interfere within the minimum detection limit of 0.01 ppm SO_2. However, 100 ppm NO_x and 100 ppm CO produced positive interferences of 0.01 and 0.02 ppm SO_2, respectively. The sulfuric acid-chromic acid bath which had been previously used to wash the impingers also gave a positive interference for samples collected in impingers washed in this bath. The problem was averted by replacing the sulfuric acid-chromic acid with 1:1 (v:v) nitric acid. The manufacturer of the ion chromatograph has stated that persulfite will interfere with sulfate analysis and that oxylate ion will interfere if the separatory column capacity is reduced. No problem has been noted with these two species.

The effect of age on sulfate standards and samples was investigated and it was found that sulfuric acid standards remained stable for at least fourteen weeks and the exhaust samples for at least two weeks but less than ten weeks. The actual lifetime probably lies between four and six weeks. This relatively long period of sample stability allows for some leeway in case the samples can not be analyzed immediately. The best collection efficiency was obtained when the dilute exhaust flowed at 4 ℓ/min through two bubblers in series, each containing 25 mℓ of 3 percent hydrogen peroxide maintained at ice bath temperature (0-5°C). Heated glass fiber filters are inserted in the sample line to prevent contamination of the samples and subsequent column poisoning in the ion chromatograph. The linearity of response of the ion chromatograph is maintained in the sulfate concentration range 0.5 to 100 μg SO_4^{-2} per mℓ (100 ppm). However, changing the attenuation on the ion chromatograph causes a discontinuity in the calibration curve. This discontinuity is seen as a slope change in Table 14. The standards analyzed at each attentuation obviously fall into a linear pattern even though the slopes differ. A different set of standards must therefore be run for each sensitivity setting.

TABLE 25. SULFUR DIOXIDE RECOVERY FROM CVS-TUNNEL INJECTION

Test	Nominal Flow Rate ft^3/min		SO_2 Injected		Calculated SO_2 Conc ppm	Observed SO_2 Conc ppm[b]	Percent Recovery
	SO_2	CVS	Vol. SO_2 (ft^3)[a]	Conc SO_2 (ppm)			
1	0.37	306	8.547	887	1.08	0.86	80
2	0.37	306	8.547	887	1.08	1.09	101
3	0.37	306	8.547	887	1.08	1.03	95
4	0.37	306	8.493	887	1.07	1.07	100
5	0.37	306	8.493	887	1.07	1.12	105
6	0.37	306	8.493	887	1.07	1.03	96
7	0.37	306	8.446	887	1.06	1.04	98
8	0.37	306	8.446	887	1.06	1.15	108
9	0.37	306	8.446	887	1.06	1.06	100
						Average	98 ± 8

---

[a] Volume corrected to 1 atm pressure and 68°F

[b] Corrected for background levels of sulfur dioxide (0.15 ppm)

TABLE 26. SULFUR DIOXIDE RECOVERY FROM DILUTE EXHAUST BY CVS-TUNNEL INJECTION DURING HOT FTP DRIVING CYCLE

Test	Nominal flow Rate ft^3/min		SO_2 Injected		Calculated SO_2 Conc	Observed SO_2 Conc	Percent
	SO_2	CVS	Vol. SO_2 (ft^3)^a	Conc SO_2 (ppm)	ppm	ppm	Recovery
1	0.36	298	8.257	9098	10.96	7.98	73
2	0.36	298	8.257	9098	10.96	11.34	103
3	0.36	298	8.266	9098	10.96	9.68	88
4	0.36	298	8.266	9098	10.96	10.88	99
5	0.36	298	8.266	9098	10.96	11.91	109
6	0.36	298	8.372	9098	11.11	8.65	78
7	0.36	298	8.372	9098	11.11	12.09	109
8	0.36	298	8.372	9098	11.11	13.04	117
						Average	97 ± 16

---

[a] Volume corrected to 1 atm pressure and 68°F

[b] Corrected for background levels (0.19 ppm) and vehicle baseline emissions (7.73 ppm) of SO_2

The results of the qualification experiments indicate that most (97-98 percent) of the sulfur dioxide that is injected into the CVS-dilution tunnel can be recovered with or without exhaust present.

The ion chromatographic method of sulfur dioxide analysis is a simple, sensitive, specific, and relatively rapid procedure with few interferences. No intermediate steps are involved, lessening the chance of sample loss or contamination. The ion chromatograph is sensitive to 0.01 ppm SO_2 and samples can be analyzed in 10 to 15 minutes. The difference in retention times between the various ions in the sample allows for definite peak identification. Sulfate analysis on the ion chromatograph is also unaffected by most interferences plaguing a number of other sulfur dioxide procedures.

SECTION 7

NITROUS OXIDE PROCEDURE

LITERATURE SEARCH

There are six common oxides of nitrogen: nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), dinitrogen trioxide (N_2O_3), dinitrogen tetraoxide (N_2O_4), and dinitrogen pentoxide (N_2O_5). In addition to these, there are two different oxides that have the empirical formula NO_3. Both are very reactive and have only been identified by spectroscopy as transient species.

Nitrous oxide is a colorless, nonflammable gas at room temperature with a slightly sweet taste and odor. Some synonyms are dinitrogen oxide, nitrogen monoxide, hyponitrous acid anhydride, factitious air and laughing gas. Nitrous oxide is the least reactive and noxious of the oxides of nitrogen. At room temperature it is relatively inert; but at 500°C, it decomposes to nitrogen, oxygen, and nitric oxide. At elevated temperatures, it will support combustion and oxidizes certain organic compounds and alkali metals. Nitrous oxide, N_2O, has a molecular weight of 44.01, a melting point of -90.8°C, and a boiling point of -88.5°C. It is a linear molecule with a N-N bond distance of 1.128 Å and a N-O bond distance of 11.84 Å and is isoelectronic with carbon dioxide. When inhaled, nitrous oxide may cause hysteria, insensibility to pain, or unconsciousness and therefore is used as anesthetic for minor operations, including dentistry. It is also used as a nontoxic dispersing agent in commercial whipped cream. Commercially, nitrous oxide is prepared by the thermal decomposition of ammonium nitrate, the controlled reduction of nitrites or nitrates, the slow decomposition of hyponitrites, and by the thermal decomposition of hydroxylamine (12).

The analysis of nitrous oxide has been conducted using mass spectrometry, infrared spectroscopy, and gas chromatography. Of these, the most sensitive method is gas chromatography (80).

There are three gas chromatography methods that have been used to analyze for nitrous oxide. Two of these require cold traps to collect and concentrate the sample (80). With the third technique, grap samples are collected in Tedlar plastic bags and analyzed with an electron capture detector (81).

PROCEDURAL DEVELOPMENT

The gas chromatograph operating conditions and sampling system specifications were obtained from EPA-RTP (81). A two column system with column backflush and isothermal temperature operation was constructed for the analysis. The stripper column is a 2' x 1/8" stainless steel tube filled with 10 percent OV-17 on 80/100 mesh Gas Chrom Q. The analytical column consists of a 6'x 1/8" stainless steel column packed with 120/150 mesh Proapak Q. A series of two six-port valves and timers is used to direct the sample flow through the columns. The samples are then analyzed with an electron capture detector. Since this method has been successfully applied to automotive exhaust, no other significant effort was applied to the procedural development. A description of the analytical system and the adapted procedure is presented as an appendix to this report.

VALIDATION EXPERIMENTS

Several experiments were conducted to validate the system for detector linearity, injection repeatability, and bag sample stability. Also, a means of calibrating the system using permeation tubes and calibration gases was investigated. The results are reported below.

Initially, a Tracor Model 412 Permeation System with an Ecocal permeation assembly was used to calibrate the instrument. The concentration of nitrous oxide could be set by changing the diluent gas flow over the permeation tube. This means of calibration can be used between the dynamic concentration range of 0.23 ppm to 6.31 ppm. However, a ghost peak was also generated with this permeation system. Efforts to eliminate this extraneous peak were unsuccessful. The permeation rate from this tube is not solely dependent on the concentration of nitrous oxide and would make this means of calibration difficult. Because of the problems associated with the permeation system, a static method of calibration was pursued. Four cylinders of calibration gas were obtained. The nitrous oxide concentrations of the cylinders ranged from 1.31 ppm to 9.90 ppm. No ghost peaks were observed and quantitative results were obtained.

Detector linearity over a wide range of concentrations is helpful and sometimes necessary when a variety of samples are to be analyzed. This is the case with gaseous bag samples. No easy method to dilute the bag concentrations into the linear range of the instrument is available. Therefore, the detector must be linear in all of the concentration ranges expected. The detector linearity for the electron capture detector was determined with calibration gases from 1 to 10 ppm (Figure 29). Sample concentrations within this range are linear with respect to the detector.

With the gas sample loop and electrical/pneumatic sample flow control, sample injections are not as subject to human error and are more reproducible than syringe sample injections. The injection repeatability for the four calibration gas standards is shown in Table 27. This table demonstrates that sample injection reproducibility is reliable with the present analytical system.

Due to the length of time required for sample collection and subsequent gas chromatograph analysis, nitrous oxide must be stable for at least several hours. The bag stability was determined by taking two random Tedlar bags filled

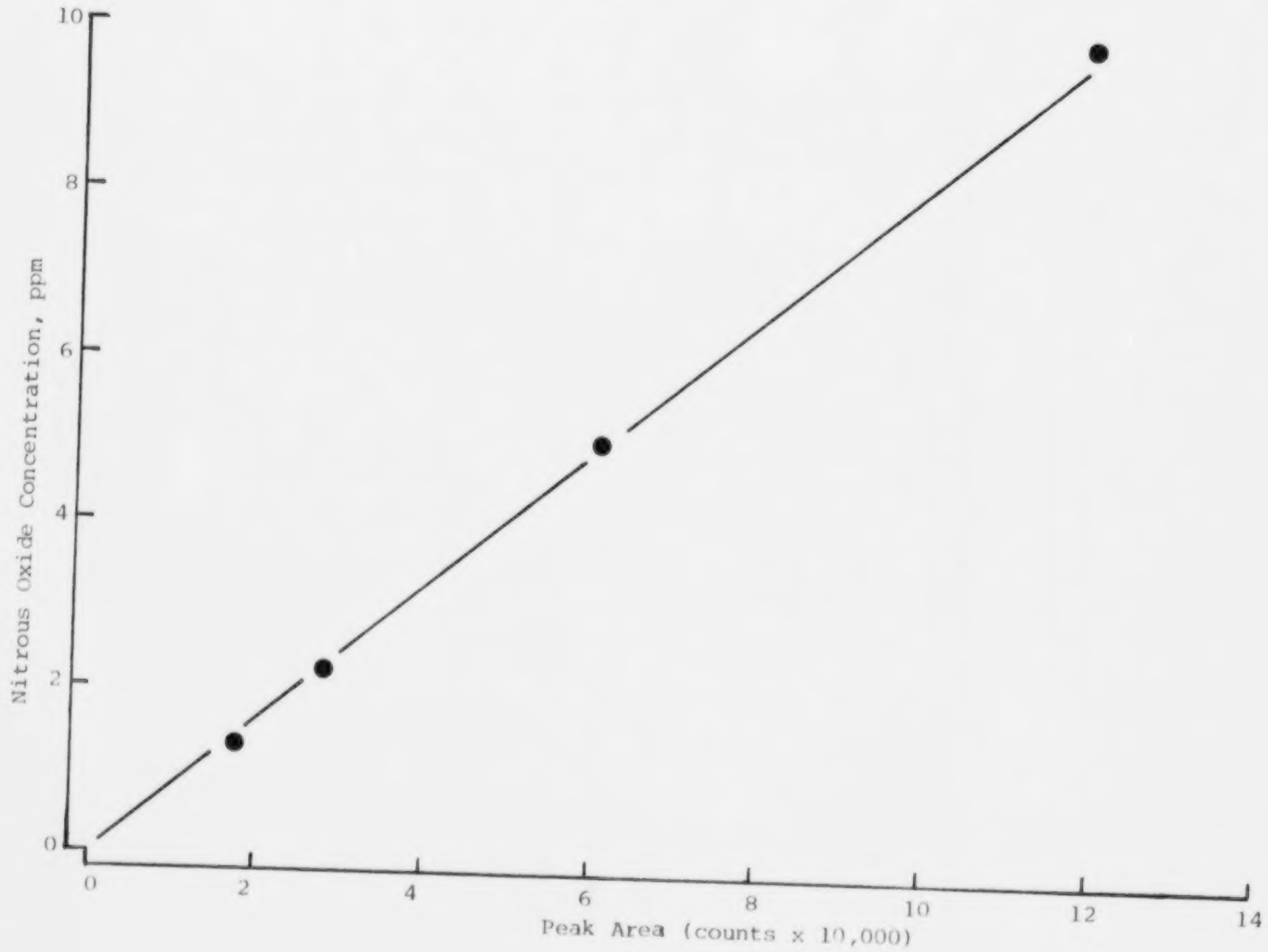


Figure 29. Detector linearity curve.

TABLE 27. INJECTION REPEATABILITY OVER THE RANGE OF DETECTOR LINEARITY

	N_2O Concentration, ppm			
	1.31	2.16	4.95	9.90
	Area			
	17935	28020	61146	118085
	17811	28759	61057	118935
	18346	28974	61004	118687
	18149	28931	61325	119448
	18319		61448	119810
				119005
Average	18112	28671	61196	118995
Standard Deviation	235	444	186	599
Coefficient of Variation	1.30	1.55	0.30	0.50

with exhaust from an emissions test. The two samples were reprocessed periodically. The first bag was processed hourly for five hours and the second bag was processed periodically for several days. The time sample decay curve for both samples is shown in Figures 30 and 31. Samples may be stored for a period of five days without adverse effects to the sample concentration.

QUALIFICATION EXPERIMENTS

Qualification recovery experiments were conducted for nitrous oxide with the dilution tunnel and with real vehicle exhaust. An aluminum cylinder containing 9000 ppm nitrous oxide in balance nitrogen was used as the source for nitrous oxide. The cylinder was named by dilution with zero nitrogen and the comparison of the diluted sample to a known standard. The exhaust in the experiments was generated from a Mercedes 240D over hot FTP (23 minute) driving cycles. The flow of nitrous oxide into the tunnel was regulated to give a concentration of approximately 10 ppm nitrous oxide in the dilution tunnel. Injections of nitrous oxide into the tunnel without exhaust gave recoveries that ranged from 95.1 to 105.6 percent with an average of 100.5 ± 3.8% (Table 28). The recovery of nitrous oxide with real vehicle exhaust ranged from 82.7 to 113.7 percent with an average of 99.6 ± 11.3 percent (Table 29). Recoveries from the injection into the tunnel without exhaust were corrected for background levels of nitrous oxide. The injections with the vehicle exhaust were corrected for the vehicle baseline emissions of nitrous oxide as well as for the background levels of nitrous oxide.

RESULTS AND CONCLUSIONS

The measurement of nitrous oxide in dilute exhaust can be conducted with gas chromatography. Dilute exhaust is collected in a Tedlar bag as a grab sample. Sample analysis of the bag sample with an electron capture detector and comparison to a set of calibration blends determines the concentration in dilute exhaust. The minimum detectable limit of this procedure is 0.01 ppm.

Detector linearity, injection repeatability, bag sample stability, and a static means of calibration were demonstrated for the system. The electron capture detector employed is linear over the range of sample concentrations expected. This enables direct sample analysis without secondary dilution. The injection repeatability for an automated sampling system with a gas sampling loop is excellent for the analytical procedure. The sample integrity is also maintained if the samples cannot be analyzed immediately. This enables minor system repairs without holding up testing.

The average CVS percent recovery is essentially 100 percent in dilute exhaust for nitrous oxide. No losses were observed with or without the vehicle. This is expected due to the inertness and stability of nitrous oxide. Sample integrity can be expected throughout the entire testing procedure and sample concentrations are not subject to the instability of the compound tested.

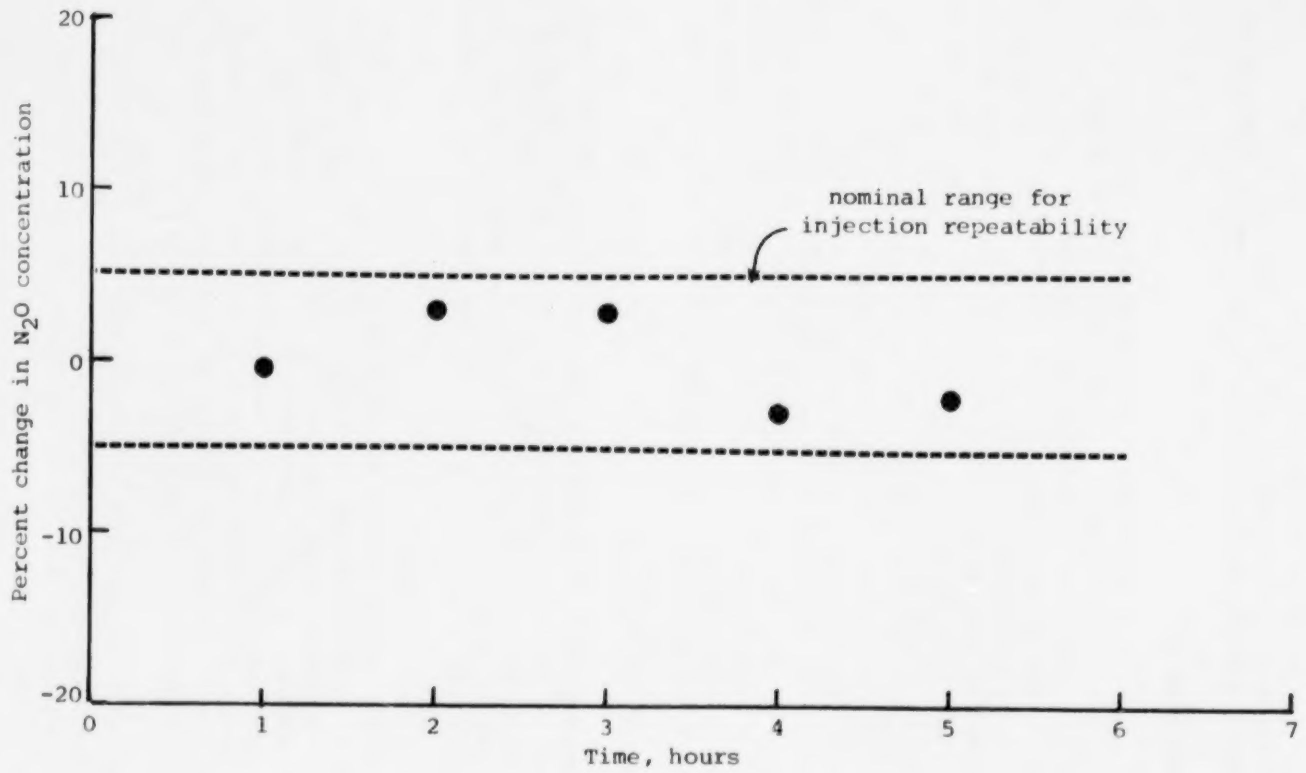


Figure 30. Sample decay curve (short term).

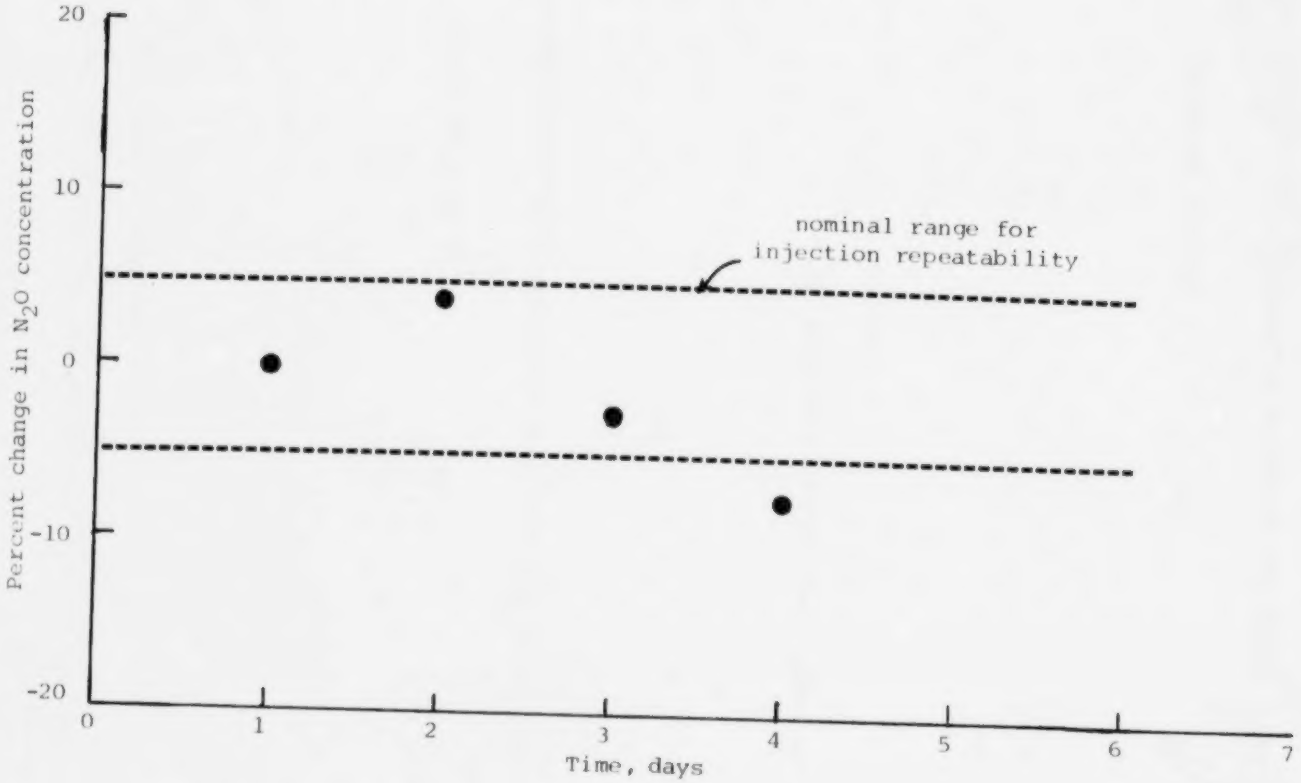


Figure 31. Sample decay curve (long term).

TABLE 28. NITROUS OXIDE QUALIFICATION EXPERIMENTS - NO VEHICLE

Run	Bag	Percent Recovery*
1	1	97.2
	2	102.5
2	1	105.6
	2	101.2
3	1	95.1
	2	101.1
	Average	100.5 ± 3.8 percent

* Corrected for background levels of nitrous oxide.

TABLE 29. NITROUS OXIDE QUALIFICATION EXPERIMENT WITH VEHICLE EXHAUST

Run	Bag	Percent Recovery*
1	1	82.7
	2	95.0
2	1	113.7
	2	108.1
3	1	93.4
	2	104.8
	Average	99.6 ± 11.3 percent

* Corrected for vehicle baseline emissions and background levels of nitrous oxide

This procedure provides a rapid and sensitive method for the analysis of nitrous oxide in dilute exhaust. A single bag sample requires about two minutes for sample loop purging and seven minutes for the automated analysis. The total analysis time is about nine minutes per sample. The automated system provides simplicity and ease of operation and makes this procedure ideal for routine analysis.

SECTION 8

HYDROGEN SULFIDE PROCEDURE

LITERATURE SEARCH

Hydrogen sulfide is a very flammable and toxic gas at room temperature and has the characteristic odor of rotten eggs. The chemical formula for hydrogen sulfide (hydrosulfuric acid or sulfureted hydrogen) is H_2S. Hydrogen sulfide is a bent molecule with a H-S-H bond angle of 93.3° and an S-H bond distance of 1.3455 Å. Hydrogen sulfide has a boiling point of -60.33°C, a melting point of -85.49°C, and a molecular weight of 34.08 (12). It is a very weak diprotic acid with dissociation constants:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad K_1 = 5.7 \times 10^{-8}$$

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^= \qquad K_2 = 1.2 \times 10^{-15}$$

Hydrogen sulfide may be detected by its odor at about 1 ppm; however, olfactory fatigue soon results and higher concentrations may not have an unduly objectionable odor. Death is caused by systemic poisoning and respiratory paralysis from exposure to high concentrations (>700 ppm).

Hydrogen sulfide is prepared commercially as a by-product from many chemical processes and by the treatment of metallic sulfides with mineral acid such as hydrochloric or sulfuric acid (12). Hydrogen sulfide produced in exhaust is probably formed by the reduction of sulfur compounds in the fuel. With an excess of oxygen, it burns to form sulfur dioxide and water:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

and with insufficient oxygen to form free sulfur and water:

$$2H_2O + O_2 \rightarrow 2H_2O + 2S$$

Hydrogen sulfide also reacts with sulfur dioxide to form free sulfur and water:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

This reaction may be significant if high levels of sulfur dioxide are produced in exhaust.

The analysis of hydrogen sulfide has been conducted with an entire spectrum of analytical methods. Some of these methods include: surface reactions on plates, tiles, tapes or filters, wet chemical, fluorimetry, infrared spectroscopy, sulfur ion selective electrode, coulometry, gas chromatography, and colorimetric (82,83). Most of these are not applicable to dilute exhaust sampling but are applicable for ambient air sampling or "on line" systems. The best applicable means of analysis for dilute exhaust is the colorimetric technique.

There are two colorimetric methods available for the analysis of hydrogen sulfide. These are the sodium nitroprusside method and the methylene blue method (84-93). The sodium nitroprusside method has a lower detection limit of about 1 ppm. This method was not considered sensitive enough for the concentrations expected in dilute exhaust. The methylene blue method, on the other hand, has a reported lower detection limit of 1-2 ppb.

The absorbing reagent is the key to successful analysis with this procedure. Hydrogen sulfide is precipitated as the sulfide in the presence of metal ions. Cadmium and zinc hydroxide, cadium sulfate, and zinc acetate have been used as the absorbing media. However, several authors have reported the oxidation of cadmium and the photochemical decomposition of cadmium sulfide. Bamesberger and Adams (85) suggested the use of 1 percent STRactan 10 as a stabilizer for cadmium absorbing solutions. On the other hand, zinc solutions do not appear to have these inherent problems. Flamm and James (93) tested all of the above absorbing reagents and found zinc acetate to be the most efficient absorbant.

PROCEDURAL DEVELOPMENT

A procedure for the analysis of hydrogen sulfide by the methylene blue method was obtained from the Project Officer under EPA Contract 68-03-2499. This procedure is a modification of the technique used by Gustafsson (86). A buffered zinc acetate solution is used as the absorbing reagent. This procedure was compared to the one recommended for ambient air sampling by Adams et al (94) which used cadmium hydroxide as the absorbing reagent. The selected analytical procedure is included as an attachment to the interim report.

The cadmium hydroxide method presented several problems. First, sulfides in alkaline solutions are easily oxidized by air. Second, cadmium sulfide is photosensitive and solutions must be protected at all time from exposure to light. The use of special glassware or aluminum soil wrappings are necessary to prevent exposure to light. The addition of a stabilizer such as STRactan 10 helps to minimize the effect of photochemical decomposition, but special handling precautions are still necessary. Cadmium solutions are hard to work with and in addition some cadmium compounds are toxic. Cadmium, cadmium oxide, cadmium sulfate, and cadmium sulfide were included in a tentative carcinogen list issued by OSHA in July, 1978. Zinc sulfide, on the other hand, is not photosensitive, the solutions are much easier to work with, and zinc compounds are not as toxic. For these reasons zinc acetate was selected as the absorbing reagent for this project.

Several authors have reported that methylene blue may be bleached by exposure to light. In order to determine what effect this might have on a developed sample, two high (18-19 μg/100 mℓ) and two low (2-3 μg/100 mℓ) concentration standards were prepared and developed for fifteen minutes. One of each concentration was then exposed to light. After developing for 15 minutes in the dark, the other two were wrapped with aliminum foil and stored in the dark. The absorbance of each was determined periodically for several weeks. The time-light exposure decay curves are shown in Figures 32 and 33. The results of these experiments are discussed in the Results and Conclusions section.

Hydrogen sulfide is readily volatilized from acidic aqueous solutions. In alkaline solutions sulfide ion may be oxidized by dissolved oxygen. The pH of the buffered zinc acetate absorbing reagent is 7.0. This reagent remains at a pH of 7 even after bubbling with dilute exhaust. Oxidation of dissolved sulfide ion does not occur rapidly at this pH. After addition of the amine solution and ferric ion to the absorbing reagent, the pH is below 2.0. At this pH, the trapped sulfide ion reacts to form methylene blue. Buffering of the absorbing reagent and subsequent change of pH in the presence of the amine solution and ferric ion minimizes the losses due to oxidation or volatilization.

There are two possible methods available for generating a Beer's Law plot for calibration. The first technique requires extensive reagent preparation and tedious titrations. A thiosulfate solution is first standarized against potassium dichromate. This standarized thiosulfate solution is used to standarize a dilute iodine solution. The standard sulfide solution concentration is then determined with an iodimetric method. Aliquots of the standarized sulfide solution are used to generate a Beer's Law curve.

The other method requires the use of a hydrogen sulfide permeation tube. The calibration curve is generated by bubbling a known concentration of hydrogen sulfide through impingers containing the absorbing solution for varying lengths of time. Generation of a calibration curve in this manner takes into account the collection efficiency of the impingers. This method is quick, efficient and more consistent with the way the samples are actually taken. It also enables the generation of a daily calibration curve without being manpower intensive.

The calibration curve for methylene blue is shown in Figure 34. This curve was determined for a standarized suflide ion solution on two separate occasions and follows Beer's Law at low concentrations. After about 70 $\mu g S^{=}$/100 mℓ, the curve begins to deviate from Beer's Law. Concentrations of hydrogen sulfide in dilute exhaust are expected to stay well within the linear range of the calibration curve.

VALIDATION EXPERIMENTS

After selecting an analytical method, validation experiments were conducted to determine the necessary sampling and procedural parameters. These experiments included trapping efficiency, calibration curve linearity, and interferences from dilute exhaust. Since the methylene blue procedure is a well documented analytical technique, only simple experiments were con-

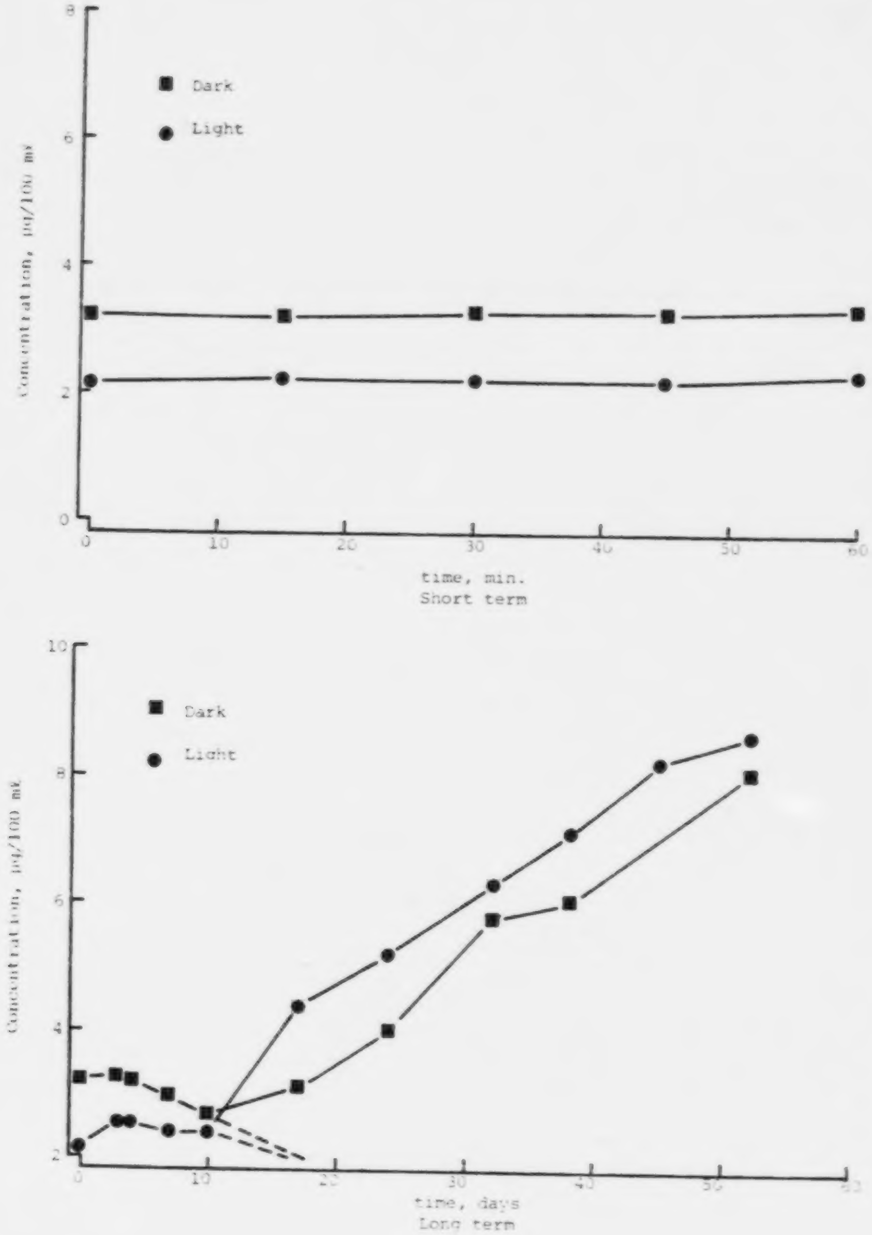


Figure 32. Time-Light exposure study low concentration H_2S.

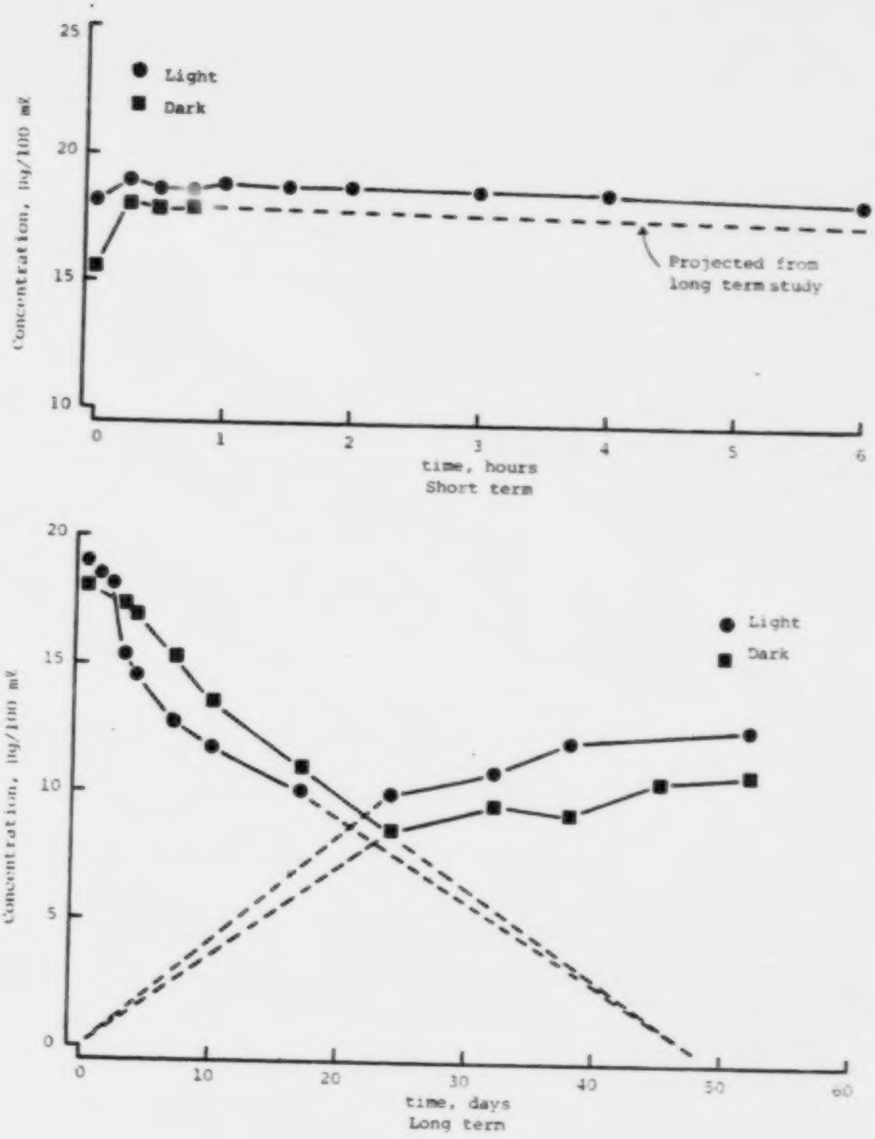


Figure 33. Time-Light exposure study high concentration H_2S.

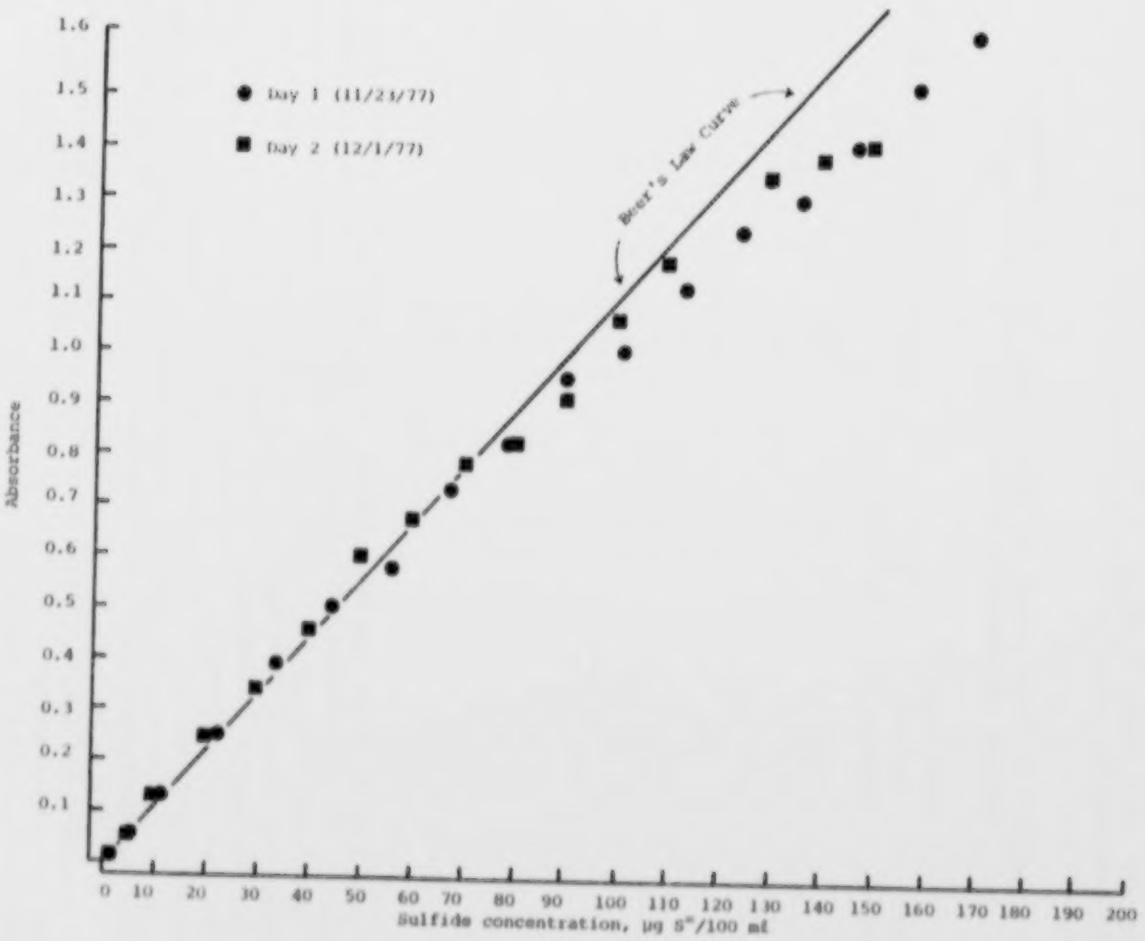


Figure 34. Beer's Law plot for methylene blue.

ducted to verify other procedural parameters. Collection efficiency and other sampling parameters were determined with a series of experiments. The first experiment determined the collection efficiency at room temperature (23° to 26°C). A 5 ppm concentration of hydrogen suflide was passed through the absorbing reagent at 1.0 and 4.0 ℓ/min. The experiment was then repeated with a sample flow of 4.0 ℓ/min and an absorbing reagent temperature of 0° to 5°C. This temperature was achieved by immersing the impingers in an ice bath. The data for this study is shown in Table 30. Sample flow rate and absorbing reagent temperature did not have a measurable effect on the collection efficiency.

TABLE 30. THE EFFECT OF SAMPLE FLOW RATE AND ABSORBING REAGENT TEMPERATURE ON THE COLLECTION EFFICIENCY

Test Number	Absorbing Reagent Temp., °C	Sample Flow Rate		Percent H_2S Collected per Bubbler		
				1	2	3
1	23	1.0		98.0	1.7	0.3
2	23	1.0		98.2	1.3	0.5
			Avg.	98.1	1.5	0.4
1	25	4.0		96.4	3.2	0.4
2	25	4.0		96.4	3.0	0.5
3	25	4.0		95.7	3.8	0.5
4	25	4.0		95.9	2.5	1.6
			Avg.	96.1	3.1	0.8
1	0	4.0		95.0	5.0	---
2	0	4.0		93.9	5.3	0.8
3	0	4.0		92.8	6.2	0.9
4	0	4.0		92.7	6.3	0.9
			Avg.	93.6	5.7	0.9

The interferences for this procedure are also well documented. In an attempt to find the sources of these interferences, several experiments were conducted. The first experiment involved the interferences produced with only the absrobing reagent. A series of calibration gases were passed through the absorbing reagent. These gases were 495 ppm carbon monoxide, 2.0 percent carbon dioxide, nitrogen dioxide, and a 5 ppmC hydrocarbon blend. These were compared to the background air and a blank with no gas bubbled through it. Each gas was bubbled at 4.0 ℓ/min for twenty minutes and developed for methylene blue. No interference from these gases was observed.

A second experiment investigated the interferences from individual exhaust gas components on a sulfide ion doped absorbing reagent. The gases used were carbon monoxide, carbon dioxide, compressed air, a hydrocarbon blend, sulfur dioxide and NO_x. Each of these gases were passed through a separate impinger filled with the doped absorbing reagent for twenty minutes at 4.0 ℓ/min. These were then compared to the doped absorbing reagent after development of methylene blue. Table 31 shows the results of this experiment. NO_x at 3000 ppm and sulfur dioxide at 5 ppm were found to quench the production of methylene blue.

TABLE 31. THE EFFECT OF INDIVIDUAL EXHAUST COMPONENTS ON THE DEVELOPMENT OF METHYLENE BLUE

Gas	Sample	Gas Conc., ppm	Absorbance	Methylene Blue Apparent Sulfide Ion Conc., μg/mℓ
Doped absorbing reagent	1		0.716	0.646
	2		0.708	0.638
Carbon dioxide	1	29,900	0.711	0.641
Carbon monoxide	1	2,709	0.704	0.634
Doped absorbing reagent	1		0.552	0.492
	2		0.560	0.500
Air	1		0.574	0.513
Hydrocarbon	1	168	0.554	0.494
Sulfur dioxide	1	5	0.461	0.408
NO_x	1	3,460	0.247	0.213
Doped absorbing reagent	1		0.648	0.582
	2		0.654	0.587
NO_x	1	315	0.666	0.599
	2	315	0.621	0.557
Sulfur dioxide	1	5	0.484	0.429
	2	5	0.533	0.475

A third experiment was designed to check the interference of anions in the development of methylene blue. Sodium salts of sulfate, thiosulfate, and bisulfate ions were used. Each of these anions was added to separate solutions of sulfide ion doped and undoped absorbing reagent. The solutions were then developed for methylene blue and compared to the doped absorbing reagent. Thiosulfate and bisulfate was investigated to determine the specific source of the sulfur dioxide interference. The results are shown in Table 32. Only bisulfate ion and thiosulfate ion caused the negative interference.

Finally, an additional experiment was conducted to help determine the source of sulfur dioxide interference. Approximately 2.5 ft^3 of 5 ppm sulfur dioxide was passed through an impinger filled with the zinc acetate absorbing reagent. This operation was then repeated six times. A 1 mℓ aliquot of the standard sulfide ion solution was added to two of these impingers. To two others, 5 mℓ were added. All six were developed for methylene blue. These were then compared to similar concentrations of sulfide ion solution doped absorbing reagent that did not undergo sulfur dioxide bubbling. These values are shown in Table 33. Again, the absorbance for methylene blue was decreased by the presence of sulfur dioxide.

TABLE 32. THE EFFECT OF ANIONS ON THE DEVELOPMENT OF METHYLENE BLUE

Anion	Sample	Absorbance	Apparent Sulfide Ion Conc., μg/mℓ
		doped with hydrogen sulfide	
Sulfate ion	1	0.238	0.205
	2	0.241	0.207
Thiosulfate ion	1	0.207	0.177
	2	0.211	0.181
Bisulfate ion	1	0.239	0.206
	2	0.231	0.198
Doped absorbing reagent		0.241	0.207
		undoped	
Sulfate ion	1	0.001	
	2	0.000	
Thiosulfate ion	1	0.009	
	2	0.004	
Bisulfate ion	1	0.007	
	2	0.005	

TABLE 33. THE EFFECT OF SULFUR DIOXIDE INTERFERENCE ON THE DEVELOPMENT OF METHYLENE BLUE

Sulfide ion added, mℓ	Absorbance	Apparent Sulfide ion Conc., μg/mℓ
	Sulfur dioxide passed through absorbing reagent	
1	0.067	0.055
1	0.070	0.057
5	0.463	0.410
5	0.326	0.284
0	0.002	0.000
0	0.006	0.000
	No sulfur dioxide passed through absorbing reagent	
1	0.082	0.067
5	0.583	0.521

QUALIFICATION EXPERIMENTS

A Mercedes 240D was used in the qualification experiments for hydrogen sulfide. The baseline emission rate for this vehicle was below the detection limits for the analytical procedure. This baseline was established from three separate hot FTP driving cycles. Hydrogen sulfide was injected into the CVS-tunnel system with and without vehicle exhaust. The concentration of hydrogen sulfide injected into the tunnel was 909 ppm. The flow of hydrogen sulfide into the tunnel was adjusted to give a diluted concentration of approximately 1 ppm. With the vehicle present, the hydrogen sulfide was injected into the raw exhaust stream as it entered the dilution tunnel. Samples were taken from the dilute exhaust stream and passed through a buffered zinc acetate absorbing reagent. The samples were treated with an amine solution and a ferric ion solution and then analyzed with a Beckman spectrophotometer.

Injections of hydrogen sulfide into the tunnel without exhaust gave recoveries that ranged from 85.0 to 96.5 percent with an average of 90.3 percent (Table 34). Initial experiments for the recovery of hydrogen suflide in the presence of vehicle exhaust gave recoveries from 60 to 65 percent. A second set of experiments with injections of hydrogen suflide into the dilution tunnel with vehicle exhaust was carried out. In this experiment five samples were collected and treated with 6 mℓ of ferric ion solution while six others were treated with 2 mℓ of ferric ion solution (Table 35). The samples that were treated with 6 mℓ of ferric ion solution gave recoveries that ranged from 84.1 to 95.6 percent with an average of

TABLE 34. HYDROGEN SULFIDE RECOVERY - NO EXHAUST PRESENT

Nominal Flow Rate, ft^3/min H_2S Blend	CVS	Run	Sample	Calculated ppm H_2S Dilute	Observed ppm*	Percent Recovery H_2S
0.375	302	1	1	1.13	0.96	85.0
0.375	302	1	2	1.13	0.99	87.7
0.375	302	1	3	1.13	1.09	96.5
0.372	302	2	1	1.12	0.98	90.0
0.372	302	2	2	1.12	1.02	87.3
0.375	302	3	1	1.13	1.02	90.2
0.375	302	3	2	1.13	1.07	94.6
0.375	302	3	3	1.13	1.03	91.1
					Average	90.3 ± 3.8

---

* Corrected for background levels of H_2S

90.6 percent. The samples that were treated with 2 mℓ of ferric ion solution gave recoveries that ranged from 57.8 to 80.8 percent with an average of 70.7 percent. Two mℓ of ferric ion solution had previously been found to be sufficient in the production of methylene blue in the presence of exhaust from gasoline powered vehicles. This was also the amount of ferric ion used in the previous diesel recovery tests. The recoveries were approximately 20 percent higher when 6 mℓ of ferric ion were used. The recovery of 90 percent using the 6 mℓ of ferric ion is also equal to the recovery from the tunnel when exhaust is not present.

Additional tests were performed using different amounts of ferric ion solution. The test using 2 and 6 mℓ of ferric ion solution was repeated on eight other exhaust samples. Four were treated with 2 mℓ of ferric ion while the other four were treated with 6 mℓ of ferric ion. The four treated with 6 mℓ gave recoveries of 19 percent higher than the four treated with 2 mℓ. Recoveries averaging higher than 90 percent could not be obtained using more than 6 mℓ of ferric ion solution. The recovery experiments without vehicle exhaust were repeated and no difference was found when 2 or 6 mℓ of ferric ion were used. Several laboratory experiments were conducted to try to determine what chemical species were involved in this phenomenon, however, no conclusive results were obtained.

Ninety percent of the hydrogen sulfide injected into the CVS-dilution tunnel can be recovered from the dilution tunnel with or without exhaust present. Six mℓ of ferric ion solution must be used to obtain maximum recoveries when diesel exhaust is present.

TABLE 35. EFFECT OF FERRIC ION SOLUTION ON HYDROGEN SULFIDE RECOVERY FROM DILUTE EXHAUST

Nominal Flow Rate, ft^3/min H_2S Blend	CVS	Run	Sample	Calculated ppm H_2S Dilute	Observed ppm	mℓ Ferric Ion Added	Percent Recovery H_2S
0.367	296	1	1	1.13	0.75	2	67.1
0.367	296	1	2	1.13	0.83	2	74.3
0.375	297	2	1	1.15	0.66	2	57.8
0.375	297	2	2	1.15	0.79	2	69.2
0.377	296	3	1	1.16	0.86	2	74.8
0.377	296	3	2	1.16	0.93	2	80.8
						Average	70.7 ± 7.8
0.367	296	1	3	1.13	0.94	6	84.1
0.375	297	2	3	1.15	1.04	6	91.1
0.375	297	2	4	1.15	1.07	6	93.7
0.377	296	3	3	1.16	1.10	6	95.6
0.377	296	3	4	1.16	1.02	6	88.7
						Average	90.6 ± 4.5

---

* Corrected for background and baseline levels of H_2S

RESULTS AND CONSLUSIONS

The measurement of hydrogen sulfide in dilute exhaust can be conducted with a colorimetric technique. Hydrogen sulfide is trapped in a buffered zinc acetate solution. Upon treatment with N, N dimethyl-para-phenylene diamine sulfate, and ferric ammonium sulfate, cyclization occurs to form methylene blue. The analysis is conducted spectrophotometrically at 667 nm. The minimum detectable concentration is 0.01 ppm.

Several experiments were conducted to determine the interferences and their sources in the analysis of hydrogen sulfide. Individual exhaust gas components such as carbon dioxide, carbon monoxide, and hydrocarbons show no effect on the absorbance of methylene blue. NO_x showed a negative interference only at concentrations ten times higher than that expected in dilute exhaust. Sulfur dioxide also shows a negative interference at 5 ppm. To determine the source of the sulfur dioxide interference, several experiments were conducted. These experiments were discussed in a previous section. In all cases with sulfur dioxide present, the absorbance of methylene blue was decreased. Also, a broad peak was observed from 525 nm to 675 nm in the visible region of the spectrum. The presence of bisulfate ion and thiosulfate ion produced the same effect. Bisulfate ion can be produced from sulfur dioxide by the simplified reaction:

$$SO_2 + H_2O \longrightarrow HSO_3^- + H^+$$

Thiosulfate ion forms bisulfate ion in strongly acidic solutions:

$$S_2O_3^= + H^+ \longrightarrow HSO_3^- + S$$

Sulfate ion shows no interference.

The presence of sulfur dioxide in the absorbing reagent apparently quenches the production of methylene blue from hydrogen sulfide. Sulfur dioxide acts as an oxidizing agent toward hydrogen sulfide (free sulfur is formed) and as a reducing agent toward methylene blue, an oxidation-reduction indicator. Sulfur dioxide dissolves in water to form sulfurous acid. Since the presence of bisulfate ion produces a similar interference, the decrease in the absorbance for methylene blue is probably due to this reaction. The elimination of the sulfur dioxide interference is not an easy task. It should be recognized, however, that an apparent decrease in concentration of hydrogen sulfide is observed when sulfur dioxide is present.

The sampling parameters used for the collection of hydrogen sulfide in dilute exhaust were determined partly by necessity and partly by consistency. The sample flow rate of 4.0 ℓ/min was selected to insure a sufficient sample for analysis although the lower flow rate showed a slightly better collection efficiency in the first bubbler. The use of an ice bath to cool the absorbing reagent was selected for simplicity and consistency with the other analytical procedures which require an ice bath. The absorbing reagent temperature produces little or no effect on the collection efficiency for ambient temperature sampling, but sample breakthrough is possible at exhaust gas sampling temperatures greater than ambient conditions. Two impingers filled with buffered zinc acetate absorbing reagent are necessary for complete sample recovery. These parameters are sufficient to collect sample concentrations within the detection limits of the procedure from dilute exhaust.

Hydrogen sulfide qualification experiments revealed average recoveries with or without exhaust present of 90 percent. Other experiments revealed that in the presence of the diesel exhaust higher recoveries are obtained when 6 mℓ of ferric ion solution are used instead of the usual 2 mℓ.

The effect of light on the stability of methylene blue was determined for four samples over a period of weeks. Both concentrations were stable for about two days whether exposed to the light or kept in the dark. The high concentration samples required a slightly longer time to develop (30 minutes) than the low concentration samples. Both concentrations exhibited a steady decay with time after the initial development. The sample decay was independent of the exposure to light. At 10 days for the low concentrations and 20 days for the high concentrations, an increase in the apparent concentration was observed. Inspection of the entire wavelength extinction curve showed that the absorbance was no longer due to methylene blue but some other constituent in the solution. No attempts were made to specifically define the source of this absorbance. However, the solutions were found to be stable in the light for at least several hours after development. If samples cannot be processed by this time, it is recommended that they be discarded because of the difficulty in preserving the sample integrity.

Two possible absorbing reagents were compared to determine the best one for the analysis. Zinc acetate was selected rather than cadmium hydroxide. Ease of use, reduced toxicity, and photochemical stability were the criteria for this selection.

This procedure provides a sensitive method for the analysis of hydrogen sulfide in dilute exhaust. A single sample requires five to ten minutes to add the reagents, thirty minutes to develop, and three to five minutes to analyze the sample. Absorbing reagent stability helps to simplify the analysis and makes this procedure ideal for analyzing a large number of samples.

SECTION 9

AMMONIA PROCEDURE

LITERATURE SEARCH

Ammonia is a colorless, corrosive, and weakly alkaline gas with a distinctive pungent odor. It has a molecular weight of 17.03, a boiling point of -33.35°C (1 atm), and a freezing point of -77.7°C (1 atm). The ammonia molecule is pyramidal in shape with N-H and H-H bond distances of 1.016 and 1.645 Å, respectively. The H-N-H bond angle is 106.67°. Ammonia is soluble in water, ethanol, methanol, chloroform, and ether. The basic nature of ammonia allows it to react with protonic acids to form water soluble ammonium salts. It also reacts to form stable metallic complexes. Chemically, ammonia is a highly associated, stable gas with only slight dissociation at 840-930°C and atmospheric pressure. The toxicity level of ammonia for humans is about 1700 ppm with an exposure of less than 30 minutes; however, the 1968 American Conference of Governmental Industrial Hygienists recommended a threshold limit of 50 ppm, the amount to which most workers may be exposed to repeatedly, day after day, without adverse affects. Ammonia poisoning is not necessarily a serious health hazard though its odor is perceptible at 20-50 ppm (12, 95, 96). Commercially, ammonia is produced by the Haber Process according to the reaction:

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$$

The reaction is carried out at 400-450°C and 200-600 atm over a specially prepared catalyst composed of iron, potassium oxide, and aluminum oxide. The most extensive use of ammonia in industry is in soil fertilization. It is also widely used to manufacture nitric acid via the Ostwald process (12, 96).

A number of methods for ammonia analysis are available; however, most of these methods are subject to interferences, especially from volatile amines. These interferences affect a number of colorimetric procedures. Nessler's reagent is sensitive to formaldehyde, alcohols, organic compounds, amines, sulfides, acetone, and aldehydes (97). Distillation is necessary to remove these interferences. The indophenol method is more sensitive than Nessler's (98), but it too suffers from contamination by formaldehyde, SO_2(10:1), Fe, Cr, Mn, and Cu (99). During color development pH must be carefully controlled for reliable results (98). Another highly sensitive procedure is the pyridine-pyrazalone method. It is very involved and is susceptible to interference from some cations at high concentrations (100). A direct colorimetric method for ammonia analysis involves collection in a neutral solvent (dioxane) containing a quinone and subsequent absorbance measurement at 480 nm on a spectrophotometer. The major drawback of this procedure is that one of the reagents, ∂-(benzenesulfonamide)-p-benzoquinone, must be synthesized, purified, extracted with benzene, and recrystalized before use (101). As with the colorimetric methods, the most serious weakness of titrimetry methods is the large number of interferences. The Kjeldahl procedure includes a distillation step, but this does not eliminate the interference from volatile amines because they, too, distill over. The classical titrimetry methods, acidimetry, complexometry, oxidimetry, and formal titration are also used for the determination of ammonia, but they are generally limited to 10^{-4} M solutions. Several instrumental optical methods are used in ammonia analysis. These include the chloramine (102), cupriammonia complex (103), ninhydrin (104), and electroanalytical methods. Additionally, there is a method for direct measurement on a spectrophotometer with a UV (105, 106) or IR (107, 108) detector as well as a number of indirect colorimetric methods (109). Gas (110, 111) and paper (112) chromatography have been employed successfully for some applications. A number of electrochemical techniques have also been developed for ammonia analysis. Among these are amperometry, polarography, and coulometric acidimetry, and oxidation (113,114). Interferences again pose a problem with these procedures. The specific ion electrode for ammonia is a relatively rapid and direct electrochemical method for determination of ammonia. However, since a longer equilibration time (about 20 minutes) is required for low NH_3 concentrations, the ammonia gas tends to escape from the basic solution. This long equilibration time causes unreliable results in the concentration range of interest (115). Volatile amines interfere with analysis (116), and the hydrophobic membrane of the electrode has been found to deteriorate in 2 to 3 weeks (115).

Both gasometric (117-119) and gravimetric (118, 120, 121, 122) techniques are not sensitive enough for trace analysis, and the chemiluminescent procedure is more involved than is practical (123, 124). The disadvantage of an enzymatic method reacting ammonia, an α-keto ester, and reduced nicotinamide adenine dinucleotide (NADH) is the high cost of NADH (101).

Ammonia has been quantitatively measured in dilute automotive exhaust using an ion chromatograph. This procedure is free from many of the common interferences that plague the classical methods. The short analysis time (10-15 minutes) makes it a prime candidate for ammonia measurement.

PROCEDURAL DEVELOPMENT

The procedure chosen for the analysis of ammonia involves the use of a new type of liquid chromatograph called an ion chromatograph. Ion chromatographic analysis is direct, relatively rapid (15-20 minutes), and sensitive to 0.01 ppm NH_3. Heavy metals will contaminate the system, and sodium and potassium ions interfere with ammonia detection at 2 ppm and 0.5 ppm, respectively. However, the most common and troublesome interferences, volatile amines, do not affect ammonia analysis on the ion chromatograph. The standards made up in water and the samples collected in a weak acid solution remain stable for at least a month allowing some delay time before processing. These advantages made the ion chromatograph the best choice as a means of measuring ammonia.

Very little procedural development was necessary for this method of analysis. However, instrument and sampling parameters did need to be selected. Suggested instrument variables such as type and strength of eluent, flowrate, chartspeed, and separator column size were provided with the ion chromatograph. These will change somewhat with each set of columns. Ultra pure nitric acid and distilled water have been found to give the best baseline and most rapid recovery from suppressor column regeneration. The regenerant solution is a 0.5 N NaOH solution made from reagent grade sodium hydroxide. Chartspeed was set at 12 in/hr, and the flowrate at about 40 percent of fullscale. Good separation was obtained with 6 x 250 mm separator column. A 3 x 150 mm precolumn (packed with the same resin as the separator column) was placed on line prior to the separator column to trap heavy metals and particulate. If these contaminates get past the precolumn they will poison the separator and suppressor columns. The precolumn can be cleaned weekly with a strong acid solution, as can the separator column if resolution deteriorates.

The sampling parameters were determined as part of the validation experiments. A sampling rate of 4 ℓ/minute at ice bath temperatures was found to be most efficient. Two bubblers containing 25 mℓ of 0.01 N H_2SO_4 capture over 99 percent of the ammonia passing through. A filter located between the sampling cart and the dilution tunnel, is used to prevent diesel particulate from contaminating the sampling system. The line connecting the filter to the dilution tunnel and the line connecting the filter and the sampling cart are heated to 175°F in order to prevent water from condensing in the sample line.

VALIDATION EXPERIMENTS

The first validation experiment conducted involved the selection of sampling parameters: flowrate, collection temperature, number of bubblers, and absorbing reagent. The data from these collection efficiency tests is found in Table 36. Ninety-nine plus percent of the ammonia was trapped in the first two bubblers under all test conditions. A flowrate of 4 ℓ/minute was selected to obtain the most sample without loss of sampling efficiency or physical loss of absorbing solution. Sampling at ice bath temperatures was selected to be consistent with other procedures; however, as seen in the data, room temperature sampling is also 99+ percent efficient. Two impingers containing 25 mℓ of 0.01 N H_2SO_4 as the absorbing solution are therefore used to trap 99+ percent of the ammonia. Increasing the acidity of the absorbant (0.06 N) causes interference with the ion chromatographic analysis by broadening the eluted peaks. Of significant importance is column contamination that occurs if particulate is not filtered from the sample prior to analysis. To prevent this contamination, a filter in the sample line is used. Heated lines are used to prevent condensation of water and the loss of ammonia in the sample line. The column can be poisoned by heavy metals present in the exhaust. These compounds adhere to the column resin and will

TABLE 36. NH_3 COLLECTION EFFICIENCY AS A FUNCTION OF FLOWRATE AND TEMPERATURE

Test	Flowrate (ℓ/min)	Temperature (°F)		NH_3 concentration (ppm) and percent in bubbler 1	3	3	Bubbler 1+2+3 (ppm)
			Ammonia flow diluted 1:5 with zero nitrogen				
1	2	32		17.10(99.6)	0.06(0.4)	0	17.16
2	2	32		19.51(99.5)	0.10(0.5)	0	19.61
3	2	32		18.34(95.2)	0.28(1.5)	0.64(3.3)	19.27
4	2	32		19.59(99.5)	0.06(0.3)	0.08(0.2)	19.68
			Average	18.64(98.4)	0.13(0.7)	0.17(0.9)	18.93
5	4	32		16.24(99.4)	0.02(0.1)	0.07(0.4)	16.33
6	4	32		17.40(100)	0	0	17.40
7	4	32		14.17(98.3)	0	0.24(1.7)	14.41
8	4	32		17.89(99.0)	0.11(0.6)	0.07(0.4)	18.06
9	4	32		17.79(99.9)	0.02(0.1)	0	17.81
			Average	16.70(99.3)	0.03(0.2)	0.08(0.5)	16.80
10	2	74		17.84(100)	0	0	17.84
11	2	74		17.87(98.5)	0.17(1.0)	0.10(0.5)	18.14
			Average	17.86(99.2)	0.09(0.5)	0.05(0.3)	17.99
12	4	75		18.83(99.4)	0.02(0.1)	0.10(0.6)	18.94
13	4	74		18.05(100)	0	0	18.05
			Average	18.44(99.7)	0.01(0.05)	0.05(0.3)	18.50
			Ammonia flow diluted 1:20 with zero nitrogen				
14	2	32		4.32(99.7)	0	0.01(0.3)	4.33
15	2	32		4.15(98.9)	0.02(0.5)	0.03(0.6)	4.20
			Average	4.24(99.3)	0.01(0.3)	0.02(0.4)	4.27

slowly elute causing broad, unidentifiable peaks to appear periodically. To prevent contamination, a strong nitric acid solution (1 N HNO_3) is used to wash the precolumn weekly. If the separator column becomes contaminated it is washed similarly. The lighter metals such as sodium and potassium elute within a reasonable length of time (less than 12 minutes), but they can interfere with the ammonia peak because their retention times are close to that of ammonia. Sodium, present in the water supply, interferes when its concentration exceeds 2 µg Na^+/mℓ. The tolerable limit for potassium is only 0.5 µg K^+/mℓ. Its presence is due to the incomplete rinsing of glassware washed in chromic acid solution. The absorbing solution, 0.01 N H_2SO_4, produces a small peak with the same retention time as ammonia, but a correction is made for this by running a blank sample each testing day. Filtered deionized water interferes negligibly (<0.01 ppm) with ammonia analysis.

Another variable for which validation tests were run is the ion chromatograph. The proper combination of eluent, columns, flowrate, and sample loop size are required to obtain optimum results. Nitric Acid (0.0075 N) flowing at 200 mℓ/hour allows good separation between peaks when a 3 x 150 mm precolumn, a 6 x 250 mm separator column, and a 9 x 250 mm suppressor column are used. These parameters will vary between column sets, making it necessary to check the eluent and flowrate when columns are changed. A small loop (0.01 mℓ or 0.2 mℓ) prevents the relatively small ammonia signal from being overwhelmed by the large hydrogen ion peak. An attempt was made to neutralize the acid collection medium with sodium and potassium hydroxide, but the sodium and potassium interferences were too large to make it practical. Injection repeatability figures are shown in Table 37. The mean or average for each set of peak heights and areas is represented by $\bar{x}$, the standard deviation by s_x, and the coefficient of variation in percent by Cv. The coefficient of variation serves as a comparison between injections made on the two days. This value is simply the standard deviation divided by the mean and multiplied by 100. Calculations are done using peak areas rather than peak heights becuase on the whole they were more reliable. The average variation in areas on the two days ran about 3.0 percent. A comparison was also made on the repeatability of standard preparation. Four 0.5 $\frac{\mu g\ NH_4^+}{m\ell}$ standards were made up using the same stock solution and analyzed on the ion chromatograph. The results are shown in Table 38.

TABLE 38. REPEATABILITY OF AMMONIA STANDARD

Sample	Concentration $\left(\frac{\mu g\ NH_4^+}{m\ell}\right)$	Attenuation	Height(in)	Area
1	0.50	3	0.50	28947
2	0.50	3	0.53	29821
3	0.50	3	0.52	29011
4	0.50	3	0.50	26819
			$\bar{x}$ 0.50	28650
			s_x 0.015	1284
			Cv 2.9%	4.5%

TABLE 37. INJECTION REPEATABILITY FOR ION CHROMATOGRAPH

Sample	Date	Concentration $\left(\frac{\mu g\ NH_4^+}{m\ell}\right)$	Attenuation (μmho)	Height (in)	Area
1	3-29-78	0.50	3	0.53	30990
2	3-29-78	0.50	3	0.54	30374
3	3-29-78	0.50	3	0.53	29891
4	3-29-78	0.50	3	0.53	29665
5	3-29-78	0.50	3	0.50	28947
				$\bar{x}$ 0.53	29973
				s_x 0.01	766
				Cv 2.8%	2.6%
1	5-09-78	0.50	3	0.51	24335
2	5-09-78	0.50	3	0.51	23205
3	5-09-78	0.50	3	0.51	24785
				$\bar{x}$ 0.51	24108
				s_x 0.00	814
				Cv 0.0	3.4%

The coefficient of variation for the area is 4.5 percent. Subtracting the Cv for injection repeatability, the repeatability of standard preparation is 1.5 percent. A 4.5 percent error then is to be expected from the instrument and standards. The particular combination of columns and the condition of the suppressor column determines the actual repeatability.

The ion chormatograph gives a linear response to ammonia at the sensitivity settings of 3 μmho and 10 μmho. Table 39 lists concentrations and corresponding heights and areas of points on the calibration curve. These values are plotted graphically in Figure 35. $(NH_4)_2SO_4$ standards ranging from about 0.4 to 30 $\frac{\mu g\ NH_4^+}{m\ell}$ (ppm NH_4^+) were run at the appropriate attenuations, 3 or 10 μmho. The areas recorded at 10 μmho were corrected to 3 μmho by multiplying by 10/3. Both scales show linearity but the slopes are visually different with relative values of 1.6 and 1.2 for the 3 and the 10 μmho scales, respectively. The 3 μmho scale reamins linear from at least 0.4 to 8 μg $NH_4^+/m\ell$ and the 10 μmho scale from 8 to 30 μg $NH_4^+/m\ell$.

Sample and standard stability as a function of time was another factor investigated. The sample was a background sample taken during the three bag FTP, SET-7, and FET driving cycles on May 29, 1978, and standard used for comparison (0.5 $\frac{\mu g\ NH_4^+}{m\ell}$) was prepared on May 29, 1978. It is obvious from the data presented in Table 40 that the sample and standards are stable for at least three weeks (23 days). The drop to zero ammonia and the jump to 0.02 ppm NH_3 on the thirtieth and thirty-second days, respectively, are probably due to instrument variation rather than sample degeneration. By the fortieth day (sixth week), however, the increase in ammonia concentrations is by 0.02 ppm. At this point the sample has probably begun to lose integrity. This is further confirmed by the fact that a ten week old FTP sample increased from 0.47 to 0.55 ppm NH_3 (17.0 percent) and that two thirteen week old FTP and FET samples increased from 0.08 to 0.11 ppm NH_3 (37.5 percent) and from 0.17 to 0.23 ppm NH_3 (35.3 percent). It appears that after six weeks the sample concentration begins to increase sharply, indicating a sample and standard lifetime of four to five weeks.

QUALIFICATION EXPERIMENTS

Qualification experiments were carried out using a Mercedes 240D vehicle. Hot FTP (23 minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel plus vehicle experiments. An aluminum cylinder containing 9226 ppm ammonia in balance nitrogen was used as the source of ammonia in the experiments. The flow of ammonia into the tunnel was regulated to give concentrations of 10-12 ppm ammonia in the dilution tunnel. The baseline ammonia emission level for the Mercedes 240D was 0.18 ppm. Injections of ammonia into the tunnel without exhaust gave recoveries that ranged from 74.9 to 75.5 percent with an average of 75.2 percent (Table 41).

TABLE 39. CALIBRATION CURVE FOR AMMONIA

Standard Concentration $\left(\frac{\mu g\ NH_4^+}{m\ell}\right)$	Attenuation (μmho)	Height (in)	Heights corrected to 3 μmho scale	Area	Area corrected to 3μmho scale
0.36	3	0.38		20,987	
0.50	3	0.56		33,412	
0.72	3	0.79		43,798	
1.00	3	1.17		65,530	
1.44	3	1.68		94,950	
1.50	3	1.89		101,103	
2.00	3	2.41		133,785	
3.00	3	3.57		188,785	
3.61	3	4.21		225,901	
4.00	3	4.56		238,585	
5.00	3	5.52		315,582	
7.22	3	7.50		423,980	
8.00	3	8.49		473,131	
8.00	10	2.49	8.30	141,874	472,913
10.00	10	2.93	9.77	170,430	568,100
14.43	10	3.97	13.23	228,363	761,210
20.00	10	4.78	15.93	299,706	999,020
28.86	10	6.30	21.00	409,068	1,363,560

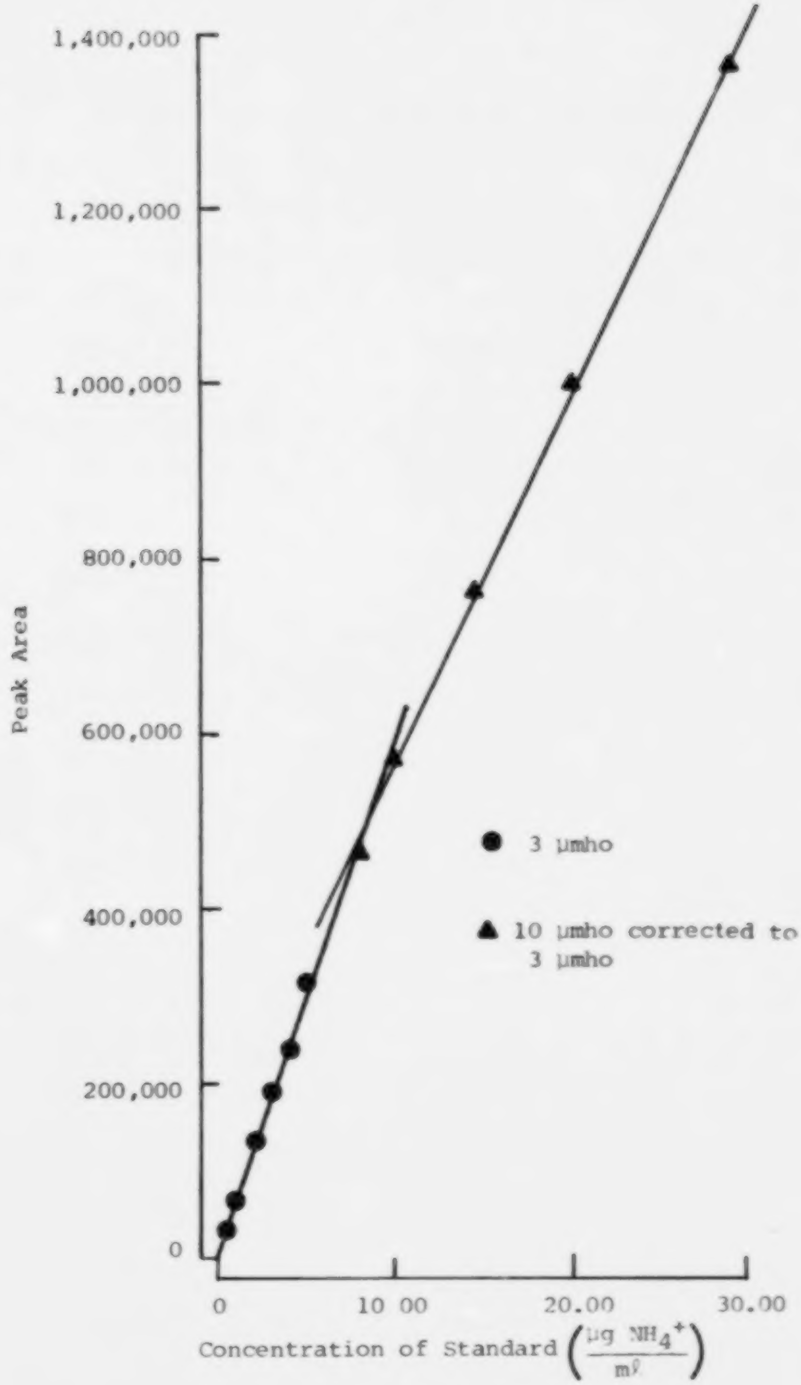


Figure 35. Ammonia calibration curve.

TABLE 40. SAMPLE AND STANDARD STABILITY AS A FUNCTION OF TIME

Date of Analysis	Age of Sample (days)	Concentration (ppm NH_3)
5-29	1	0.01
5-30	2	0.01
5-31	3	0.01
6-01	4	0.01
6-02	5	0.01
6-05	8	0.01
6-13	16	0.01
6-20	23	0.01
6-27	30	0.00
6-29	32	0.02
7-07	40	0.03

TABLE 41. AMMONIA RECOVERY FROM CVS-TUNNEL, NO EXHAUST

Test	Nominal Flow Rate ft^3/min		Ammonia Injected		Ammonia Recovered		Calculated Amount of NH_3 recovered (ppm)	Percent Recovery
	NH_3	CVS	volume NH_3[a] injected (ft^3)	Concentration NH_3 injected (ppm)	Total diluted[a] volume (ft^3)	Sample[b,c] Concentration (ppm)		
1	0.38	310	8.775	9226	7130	8.55	11.35	75.3
2	0.38	310	8.756	9226	7122	8.49	11.34	74.9
3	0.38	310	8.745	9226	7139	8.53	11.30	75.5
							Average	75.2

---

[a] Volume corrected to 1 atm and 68°F

[b] Corrected for background level of ammonia (0.06 ppm)

[c] Each value is the average of three samples taken during each test

Two separate experiments were carried out for the recovery of ammonia in the presence of vehicle exhaust. In the first experiment (Table 42) the sample lines were heated to 175°F and unheated 25 mm Fluoropore filters (0.5 μ pore size) were used to remove particulate. The recoveries ranged from 53.6 to 63.5 percent with an average of 59.5 percent. Samples taken without the filter in place gave similar results. In the second experiment (Table 43) the filter (7 cm glass fiber filter) and the sample line between the filter and the dilution tunnel were heated to 375°F. All other sampling conditions remained the same. In this experiment the recoveries were lower and ranged from 31.3 to 36.5 percent with an average of 33.1 percent. At this time, the reasons for lower recovery using the heated filter are unknown. It was expected that higher recoveries would be obtained, as was the case with the organic amines (Section 5). A twenty-five percent loss of ammonia to the dilution tunnel can be expected when sampling for ammonia at the 5-10 ppm levels. An additional fifteen percent of the sample will be lost due to the presence of exhaust when using an unheated filter to remove particulate.

RESULTS AND DISCUSSION

The ion chromatograph was chosen as the most favorable means of measuring ammonia because of the simple, direct, and rapid processing of samples. Most compounds that interfere with alternate ammonia procedures do not affect ammonia analysis on the ion chromatograph. The selectivity and sensitivity of this method warrants its use for the analysis of dilute automotive exhaust samples.

The sampling parameters providing the most efficieny collection of ammonia were selected. Twenty-five milliliters of the absorbing solution, 0.01 N H_2SO_4, is placed in each of the two bubblers in series and maintained at ice bath temperatures. Over 99 percent of the ammonia in the dilute exhaust flowing at 4 ℓ/min is captured in these two bubblers. After sample collection it is necessary to set instrument parameters to obtain good separation in the shortest time possible. These parameters, such as eluent concentration and flowrate, will depend on the particular column set in use. A 6 x 250 mm separator column has been found to resolve ammonia adequately. The 3 x 150 mm precolumn removes particulate, and the 9 x 250 mm suppressor column neutralizes the acidic eluent. With these columns installed, the eluent, 0.0075 N HNO_3, flowing at 30 percent of pump capacity, gives good ammonia resolution. A small sample loop (100 μℓ) is necessary to prevent the very broad H^+ peak from the acidic absorbing solution from obliterating the ammonia signal. The injection variability of the ion chromatograph is 3.0 percent, and for standard preparation the variation is 1.5 percent. The ion chromatogarph gives a linear response for $(NH_4)_2SO_4$ standards in the range 0.4 to 30 $\frac{\mu g\ NH_4^+}{m\ell}$, however, the attenuator is not linear between different sensitivity settings. Therefore, a different set of standards needs to be run at each attenuation. The study conducted on the effect of age on sample and standard stability showed the lifetime to be between four and five weeks. Thereafter, sharp jumps in concentration of ammonia may occur. Ammonia cannot be quantitatively recovered from the CVS-dilution tunnel with or without exhaust present. At ammonia levels of 5-10 ppm there is a twenty-five percent loss of ammonia to the dilution tunnel and an additional fifteen percent loss to exhaust.

TABLE 42. AMMONIA RECOVERY FROM DILUTE EXHAUST (NO HEATED FILTER)

Test	Nominal Flow Rate ft^3/min NH$_3$	Nominal Flow Rate ft^3/min CVS	Ammonia Injected: volume NH$_3$[a] injected (ft^3)[b]	Ammonia Injected: Concentration NH$_3$ injected (ppm)	Ammonia Recovered: Total diluted[a] volume (ft^3)	Ammonia Recovered: Sample[b,c] Concentration (ppm)	Calculated Amount of NH$_3$ recovered (ppm)	Percent Recovery
1	0.37	302	8.610	9226	6937	7.01	11.44	61.3
2	0.38	296	8.780	9226	6816	7.55	11.89	63.5
3	0.37	296	8.550	9226	6797	6.22	11.60	53.6
							Average	59.5

---

[a] Volume corrected to 1 atm pressure and 68°F

[b] Corrected for background levels (0.08 ppm) and baseline (0.18 ppm) levels of ammonia

[c] Each value is the average of three samples taken during each test

TABLE 43. AMMONIA RECOVERY FROM DILUTE EXHAUST, HEATED FILTER

Test	Nominal Flow Rate ft^3/min		Ammonia Injected		Ammonia Recovered		Calculated Amount of NH_3 recovered (ppm)	Percent Recovery
	NH_3	CVS	volume NH_3[a] injected (ft^3)[b]	Concentration NH_3 injected (ppm)	Total diluted[a] volume (ft^3)	Sample[b,c] Concentration (ppm)		
1	0.37	299	8.435	9226	6884	3.55	11.31	31.4
2	0.37	299	8.592	9226	6872	4.21	11.53	36.5
3	0.38	298	8.699	9226	6852	3.65	11.71	31.3
							Average	33.1

---

[a] Volume corrected to 1 atm pressure and 68°F

[b] Includes baseline and background correction

[c] Each value is the average of three samples taken during each test

The ion chromatograph method of measuring ammonia is an effective and efficient means of ammonia analysis in dilute automotive exhaust. This procedure is insensitive to most of the interferences plaguing other widely used methods. The ion chromatograph simplifies ammonia measurements to a one step injection, avoiding intermediate processes such as distillation, color development, or reagent preparation. The lengthiest portion of ammonia determination is the actual analysis time. This 12-30 minute analysis is relatively short for such a sensitive method (minimum detection limit is 0.01ppm NH_3). Sample and standard stability as well as linearity of response in the concentration range of interest are additional factors which make this procedure the most desirable method of measuring ammonia in automotive exhaust.

SECTION 10

ORGANIC SULFIDE PROCEDURE

LITERATURE SEARCH

The organic sulfides that are included in this analysis are carbonyl sulfide, methyl sulfide, methyl disulfide, and ethyl sulfide. The chemical formulas, molecular weights, freezing points, boiling points, and common synonyms are listed in Table 44. Carbonyl sulfide is the only sulfide of interest that is a gas at room temperature. In general, the organic sulfides are malodorous compounds that produce an unpleasant odor similar to rotton eggs. The 1968 American Conference of Governmental Industrial Hygienists made no recommendation for threshold limit values for these sulfides.

TABLE 44. LIST OF SULFUR COMPOUNDS INCLUDED IN THE ANALYSIS OF ORGANIC SULFIDES

Sulfur Compound	Chemical Formula	Molecular Weight	Freezing Point,°C	Boiling Point,°C	Synonyms
Carbonyl Sulfide	COS	60.075	-138.8	-50.2	Carbon oxysulfide
Methyl Sulfide	CH_3SCH_3	62.13	-98.27	37.3	Dimethylsulfide
Methyl Disulfide	CH_3SSCH_3	94.20	-84.72	109.7	Dimethyldisulfide
Ethyl Sulfide	$C_2H_5SC_2H_5$	90.19	-103.9	92.1	Diethylsulfide

Several gas chromatographic methods have been used for the analysis of organic sulfides originating from a wide variety of sources. A gas chromatograph with a thermal conductivity detector has been used by several workers to analyze gas odorants for mercaptans and/or sulfides (125-129); however, none of these works were concerned with trace gas analysis. Gas chromatography and mass spectroscopy were used to separate and identify low boiling sulfur compounds in crude oil (130-132). Temperature programmed gas chromatography was found to improve the separation of mercaptans and sulfides (133-135). The separation and identification of hydrogen sulfide, sulfur dioxide, mercaptans, alkyl sulfides, and disulfides in Kraft pulp digester blow gas and black liquor combustion products was accomplished using gas chromatography (136).

Carbonyl sulfide has been quantitatively measured in natural gas (137) and in carbonated beverages (138) by the use of gas chromatography. The measurement of carbonyl sulfide in carbonated beverages used an electron capture detector and had a detection limit of 0.3 ppm. Improved sensitivity in the detection of sulfur compounds in waste process gases was accomplished by concentrating the compounds on activated silica gel at -78.5°C, desorption under heat and vacuum, trapping at -96°C, and transferring to a gas chromatograph for analysis (139).

Several columns have been used to separate sulfur compounds from normally occurring atmospheric hydrocarbons, but little success has been obtained (140). A GC-microcoulometry method eliminated the interference from the hydrocarbons and was sensitive to 1 ppm mercaptan (141). A gas phase chemiluminescent reaction of ozone with organic sulfides has been considered as method of detection in monitoring low concentration of ozone and sulfur containing pollutants (142).

The detection limits for the analysis of sulfur compounds were improved greatly with the development of the Melpar flame photometric detector (FPD). The characterization of the FPD response to several sulfur compounds was carried out by Mizany (143). The FPD detector has been applied to low concentration air pollution monitoring (72), measurement of trace organic sulfides in air (144), and soil and water anlaysis (144). Permeation tubes have been used in several cases to generate continuous samples of known concentrations of various sulfur compounds (71,72). The use of Teflon throughout the gas chromatograph system has been found to minimize absorptive losses (144) and has increased sensitivity to 10 ppb (71).

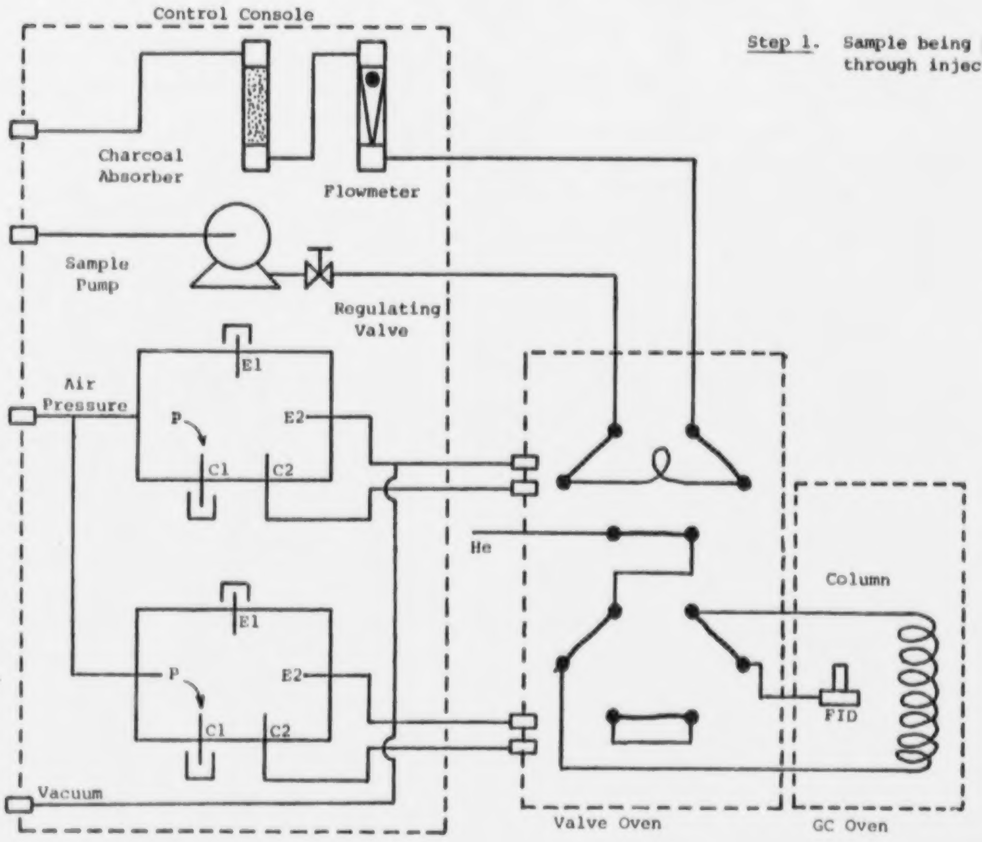
Several columns have been evaluated at several temperatures in conjunction with the Melpar flame photometric detector (77). The columns evaluated were Chromosorb T, Carbopak B-HT-100, Chromosil 310, and Deactigel. A number of other sulfur compounds have been quantitatively measured from a wide variety of sources using gas chromatography (145-151).

PROCEDURAL DEVELOPMENT

From the results of the literature search it was determined that the analysis of the organic sulfides should be conducted by the use of a gas chromatograph (GC) equipped with a flame photometric detector.

A Perkin-Elmer Model 3920 B gas chromatograph was dedicated for this purpose. The instrument has a linearized flame photometric detector (FPD) and a sub-ambient oven accessory. The sub-ambient oven accessory allows for maximum flexibility in determining GC operating conditions.

A flow schematic of the gas chromatograph analytical system used in the procedural development work is shown in Figures 36-38. The sample is purged through the gas sampling valve sample loop (Figure 36, Step 1). The values are maintained isothermally at 100°C in a valve oven. The sample is injected into the gas chromatograph after the system has been efficiently purged (Figure 37, Step 2). After all peaks of interest have eluted from the analytical column, the column is backflushed and the system is readied for the next injection (Figure 38, Step 3).


Control Console
Charcoal Absorber
Flowmeter
Sample Pump
Regulating Valve
Air Pressure
E1
E2
P
C1
C2
E1
E2
P
C1
C2
Vacuum
He
Column
FID
Valve Oven
GC Oven

Step 1. Sample being purged through injection valve

Figure 36. Proposed GC flow schematic for analysis of organic sulfides (Step 1).

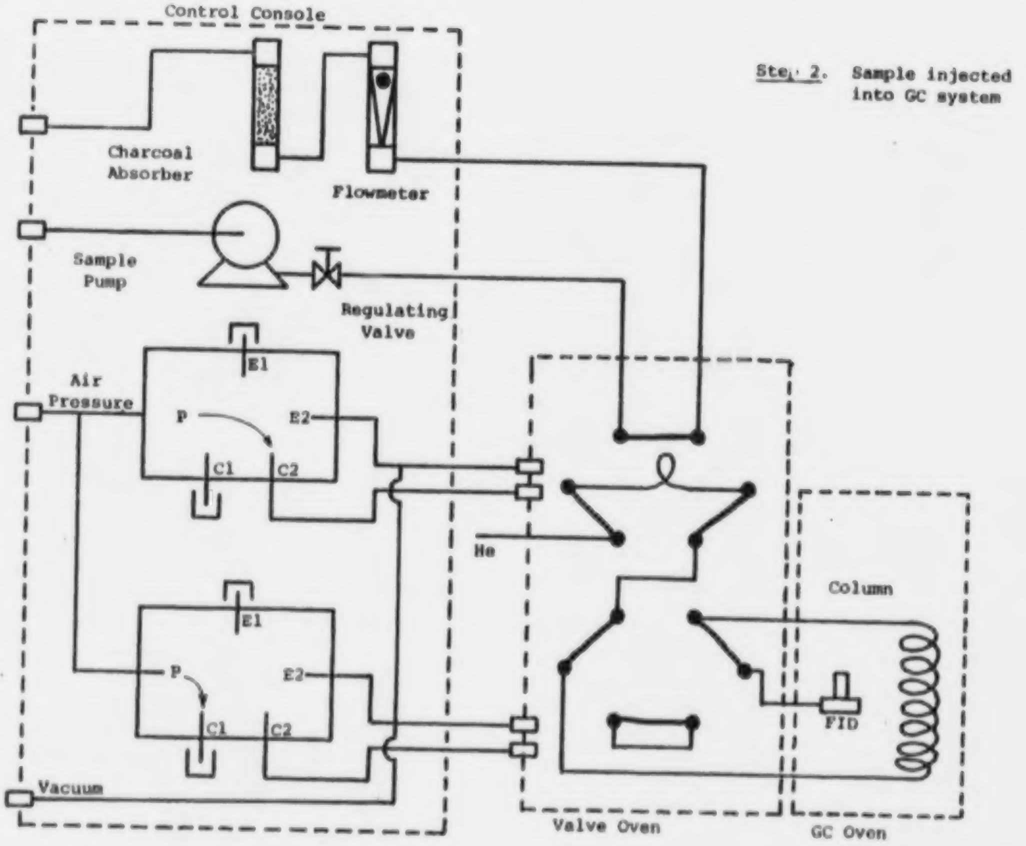
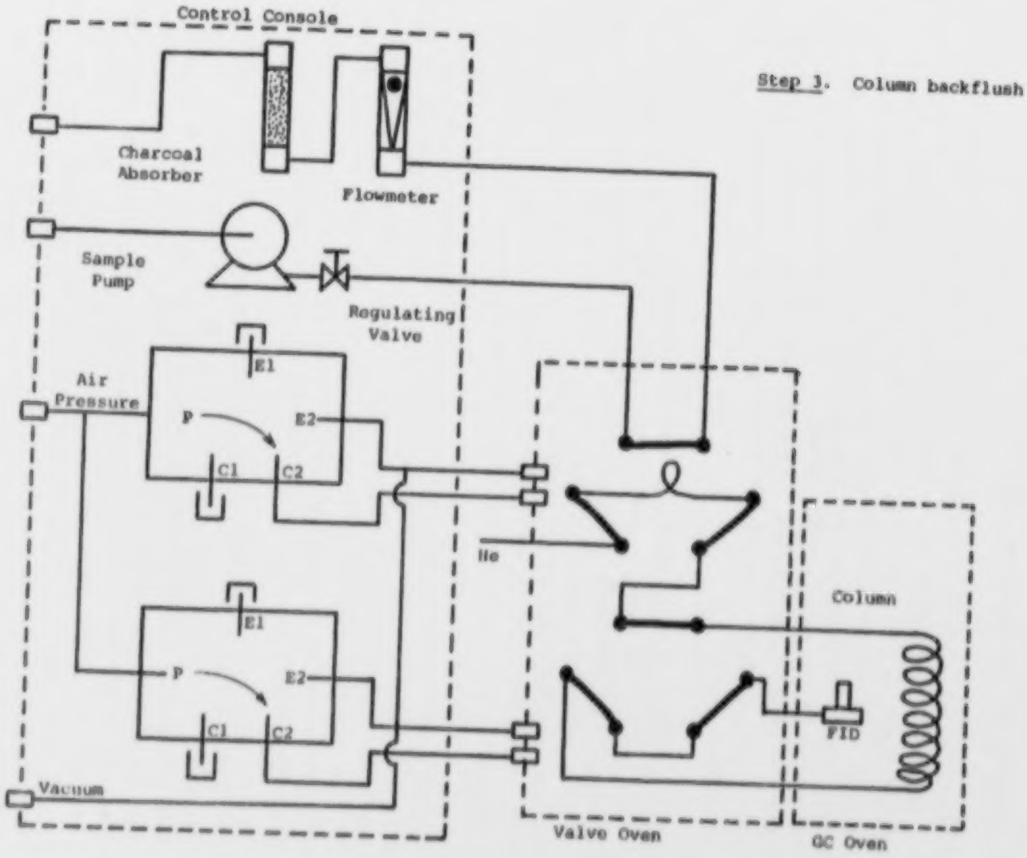

Control Console
Charcoal Absorber
Flowmeter
Sample Pump
Regulating Valve
Air Pressure
E1
P
E2
C1
C2
E1
P
E2
C1
C2
Vacuum
He
Valve Oven
Column
FID
GC Oven
Step 2. Sample injected into GC system

Figure 37. Proposed GC flow schematic for analysis of organic sulfides (Step 2).


Control Console
Charcoal Absorber
Flowmeter
Sample Pump
Regulating Valve
Air Pressure
E1
P
E2
C1
C2
E1
P
E2
C1
C2
Vacuum
He
Column
FID
Valve Oven
GC Oven

Step 3. Column backflush

Figure 38. Proposed GC flow schematic for analysis of organic sulfides (Step 3).

The column selected for the initial time was a 6' x 1/8" Teflon column packed with 60/80 Chromosil 310. Several different GC operating conditions were tried, and a preliminary set of conditions were sleected that provided an adequate separation of the four organic sulfides of interest. The separation of these sulfides is presented in Figure 39. The elution of other sulfur containing compounds is also included. Table 45 presents a list of chemical and physical characteristics of various sulfur compounds that could be present in automotive exhaust.

A lecture bottle of carbonyl sulfide, pure liquids of methyl sulfide, ethyl sulfide, and methyl disulfide, along with a Tracor Model 412 Permeation Calibration System containing all four sulfides, were used as sources for the organic sulfides in the procedural development. Permeation tubes of methyl mercaptan, ethyl mercaptan, hydrogen sulfide, and sulfur dioxide, blends of hydrogen sulfide and sulfur dioxide in aluminum cylinders with balance nitrogen, lecture bottles of hydrogen sulfide, sulfur dioxide, and methyl mercaptan, and a pure liquid of ethyl mercaptan were used in the interference checks.

Two methods of sample acquisition were considered for the analysis of the organic sulfides. One method would be to use sample bags obtained during the standard CVS testing. An alternate approach would be to use a trap packed with a material such as Tenax GC for concentrating the sample. In this manner an exhaust sample would be pulled through the trap during the entire test, thereby giving an effective sample volume of several liters rather than 5-10 mℓ. The use of the trap would increase the limits of detectability by a factor of over 1000. The collection by the use of sample bags was discarded due to the expected low concentrations of organic sulfides in exhaust and the large losses of methyl sulfide, ethyl sulfide, and methyl disulfide onto the walls of the Tedlar bags at ppb levels. Because the concentration of the organic sulfides is expected to be very low in exhaust, a number of experiments were conducted to investigate various concentration techniques that may apply to the measurement of the organic sulfides.

The first set of experiments involved the use of a U-tube type trap and was conducted using several trap volumes ranging in size from 5 to 20 mℓ. The basic flow schematic of the sampling system is shown in Figure 40. A permeation gas blend of carbonyl sulfide and methyl sulfide was used in these experiments, with the actual concentration depending on the particular experiment. Two flow rates through the traps were used: 12.0 mℓ/min (9.50 ppm COS and 4.77 ppm CH_3SCH_3) and 81.2 mℓ/min (1.40 ppm COS and 0.71 ppm CH_3SCH_3). The traps were maintained at -78°C during the sampling period. The purpose of these experiments was to see if it is possible to cold trap (at -78°C) the sulfides and then use the cold trap as a sample loop on the gas chromatograph system. Results of these experiments are presented in Table 46. Based on these results, it was apparent that the carbonyl sulfide and methyl sulfide could not both be retained under any of the trap sizes or concentrations investigated. The only condition that indicated there may be some possibility for this method was the large trap loop (20 mℓ) at the higher flow rate and lower concentration. Even in this particular case, the trapping was effective only on methyl sulfide.

GAS CHROMATOGRAPH CONDITIONS

Perkin-Elmer 3920B w/FPD 6' x 1/8" column packed with 60/80 chromosil 310, N_2 at 20 mℓ/min., oven isothermal at 0°C for 8 min and programmed to 140°C/min. at 32°C/min.

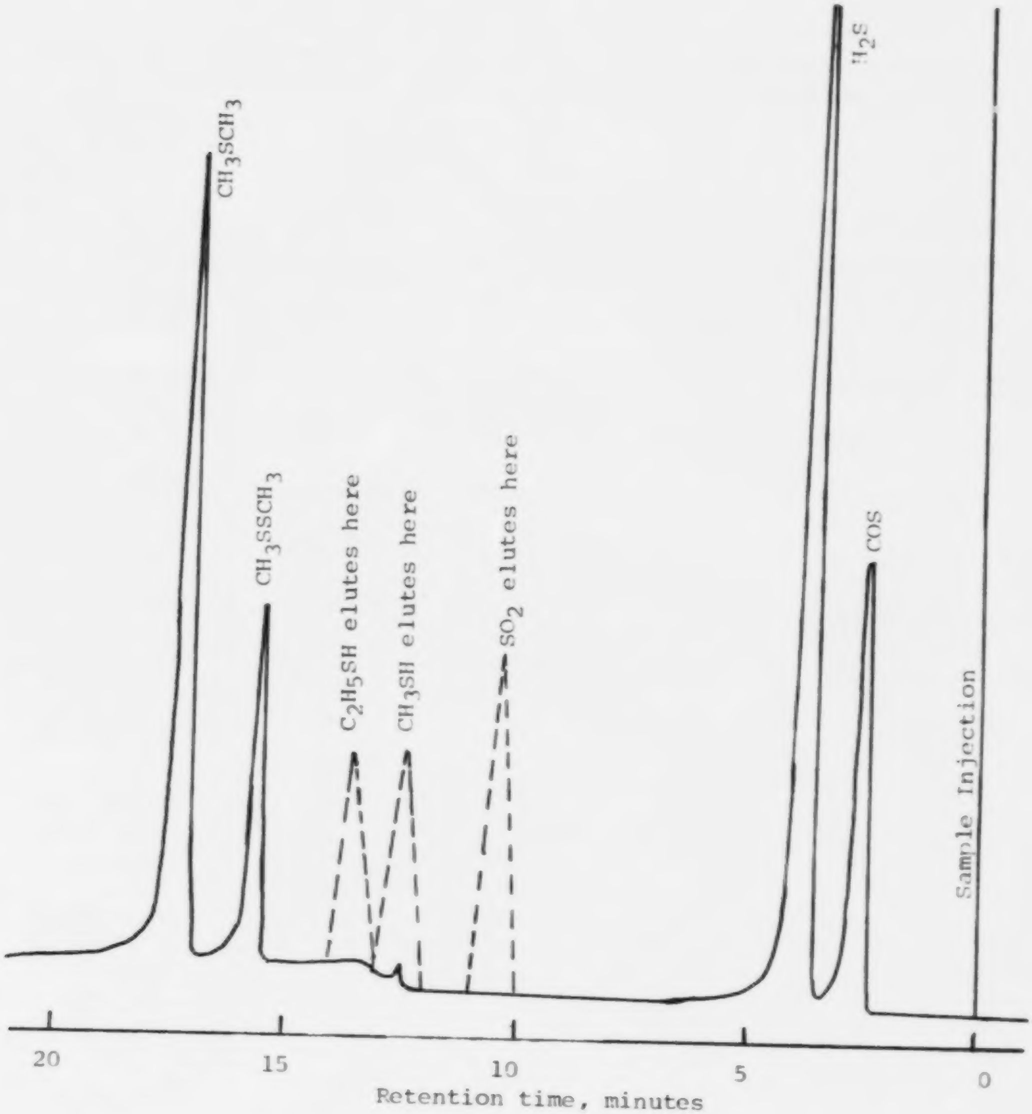


Figure 39. Gas chromatograph separation of several organic sulfides in prepared blend.

TABLE 45. LIST OF CHEMICAL AND PHYSICAL CHARACTERISTICS OF VARIOUS SULFUR COMPOUNDS POTENTIALLY PRESENT IN AUTOMOTIVE EXHAUST

Sulfur Compound	Chemical Formula	Molecular Weight	Density	Boiling Point, °C	Retention Time
Carbonyl Sulfide	COS	60.075	2.5300 g/ℓ	-50.2	2.8
Hydrogen Sulfide	H_2S	34.08	1.5392 g/ℓ	-60.3	4.2
Sulfur Dioxide	SO_2	64.063	2.927 g/ℓ	-10.0	10.5
Dimethyl Sulfide	CH_3SCH_3	62.13	0.848 g/mℓ	37.3	17.5
Dimethyl Disulfide	CH_3SSCH_3	94.20	1.0625 g/mℓ	109.7	15.8
Diethyl Sulfide	$C_2H_5SC_2H_5$	90.19	0.836 g/mℓ	92.1	----
Methyl Mercaptan	CH_3SH	48.11	0.8665 g/mℓ	6.2	12.5
Ethyl Mercaptan	C_2H_5SH	62.13	0.8391 g/mℓ	35	13.5

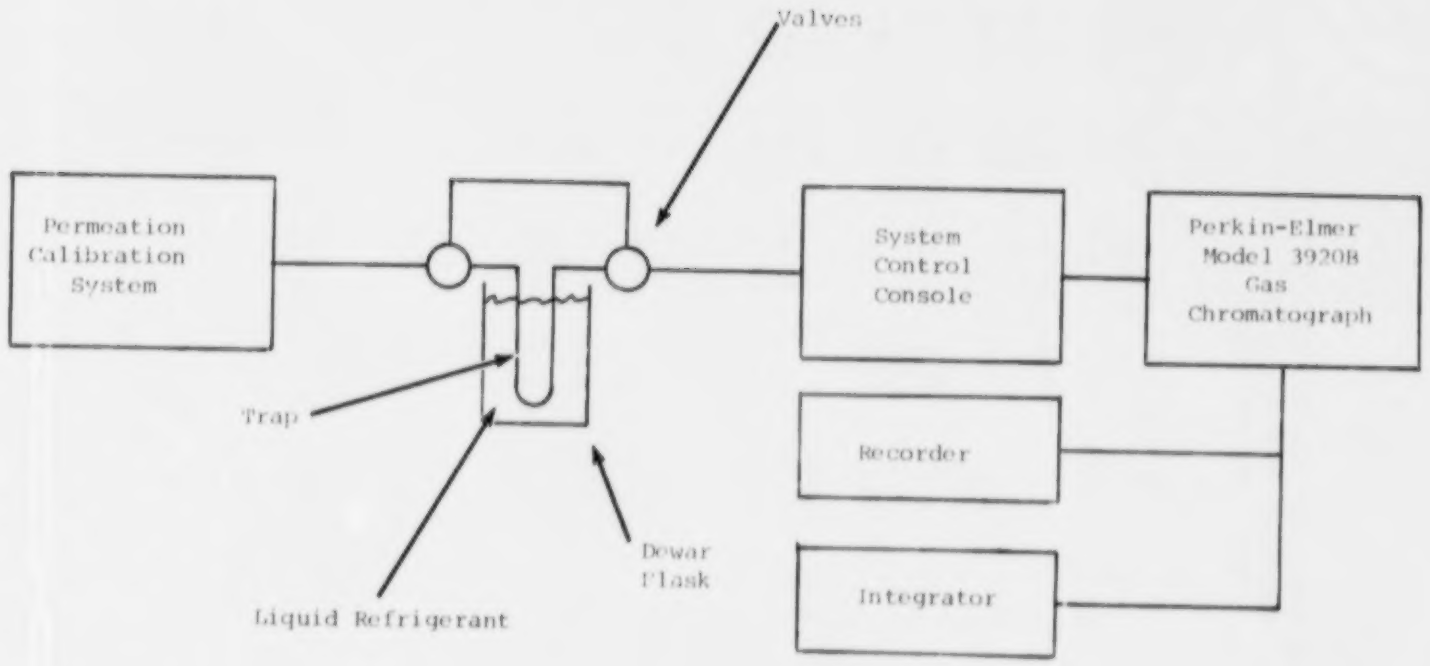

Valves
Permeation Calibration System
System Control Console
Perkin-Elmer Model 3920B Gas Chromatograph
Trap
Recorder
Dewar Flask
Integrator
Liquid Refrigerant

Figure 40. Cold trap experiment flow schematic.

TABLE 46. THE EFFECT OF COLD TRAPPING AT -78°C ON CARBONYL SULFIDE AND METHYL SULFIDE AT VARIOUS CONCENTRATIONS, FLOW RATES AND TRAP SIZES

Trap loop,mℓ	Trap Flow mℓ/min	inj.	Trap Inlet				Trap Exit	
			Conc., ppm		Peak Height		Peak Height	
			COS	CH_3SCH_3	COS	CH_3SCH_3	COS	CH_3SCH_3
5.0	12.0	1	9.50	4.77	84.5	16.1	84.2	4.1
5.0	12.0	2	9.50	4.77	84.5	16.0	84.2	13.8
				Avg.	84.5	16.0	84.2	9.0
10.0	12.0	1	9.50	4.77	84.2	13.3	84.5	1.1
10.0	12.0	2	9.50	4.77	84.2	13.4	84.5	11.4
				Avg.	84.2	13.4	84.5	6.3
15.0	12.0	1	9.50	4.77	84.2	13.3	84.9	12.6
15.0	12.0	2	9.50	4.77	84.2	13.4	84.9	13.0
				Avg.	84.2	13.4	84.9	12.8
20.0	12.0	1	9.50	4.77	85.0	14.6	84.9	0.0
20.0	12.0	2	9.50	4.77	85.0	14.4	84.9	10.0
				Avg.	85.0	14.5	84.9	5.0
5.0	81.2	1	1.40	0.71	63.0	5.2	64.9	5.2
5.0	81.2	2	1.40	0.71	63.5	5.2	65.0	4.2
				Avg.	63.2	5.2	65.0	4.7
10.0	81.2	1	1.40	0.71	63.0	5.2	63.0	4.2
10.0	81.2	2	1.40	0.71	63.5	5.2	63.5	4.2
				Avg.	63.2	5.2	63.2	4.2
15.0	81.2	1	1.40	0.71	63.0	5.2	62.0	5.0
15.0	81.2	2	1.40	0.71	63.5	5.2	62.1	4.5
				Avg.	63.2	5.2	62.1	4.8
20.0	81.2	1	1.40	0.71	63.0	5.5	65.0	0.0
20.0	81.2	2	1.40	0.71	62.0	5.0	66.0	0.0
				Avg.	62.5	5.3	65.5	0.0

One additional trap temperature was investigated prior to elimination of cold trapping as a possible concentration technique. In this experiment the trap was cooled to liquid nitrogen temperature. The results of this experiment are presented in Table 47. Only one set of concentrations (1.40 ppm COS and 0.71 ppm CH_3SCH_3) was used in this experiment. All sample loop sizes were somewhat effective in collecting the carbonyl sulfide, with a nominal collection efficiency ranging from 76 to 86 percent. The collection efficiency for methyl sulfide was slightly higher, but the repeatability was less, probably due to the low peak heights for this species. From these experiments it was apparent that cold trapping, using traps up to 20 mℓ in volume, and temperatures as low as -196°C would not quantitatively remove either carbonyl sulfide or methyl sulfide.

Efforts were then directed toward determining the feasibility of using short stainless steel cartridges packed with an absorbing material to concentration the organic sulfides. The absorption traps are lengths of stainless steel tubing 2 inches in length and 3/8" OD. The material is held in the stainless cartridge by stainless micron inserts in each of the unions on both ends. Four packing materials were selected to be evaluated at four collection temperatures. The four packing materials that were used in this experiment include Tenax-GC, Chromosorb 102, Porapak Q, and Chromosorb T. The collection efficiency of these traps was evaluated at temperatures of 20°C, 0°C, -78°C, and -196°C.

A permeation calibration gas sample containing 1.40 ppm carbonyl sulfide and 0.71 ppm methyl sulfide in a balance nitrogen gas was used for this study. The results of this study are presented in Table 48. Three of the four packings are essentially 100 percent efficient in removing both carbonyl sulfide and methyl sulfide at -78°C. These three packings were Tenax-GC, Chromosorb 102, and Porapak Q. All of the traps except Chromosorb T were effective in removing methyl sulfide at all of the temperatures investigated. Problems were encountered using trap temperatures of -196°C. At this temperature flow restrictions were noted in the trap as the test proceeded. There were also problems in desorbing traps that were stored at this temperature.

The sulfides were thermally desorbed from the traps by connecting the traps into the gas injection system with two quick connects and immediately injecting the sample into the GC system and placing the traps inside a Lindburg furnace operating at 300°C. The carrier gas upon injection flows through the loop carrying the contents of the trap into the gas chromatograph. The 300°C temperature is the temperature needed to thermally desorb the traps without causing broad sulfide peaks which result from gradual thermal desorption. The 300°C temperature is also low enough to prevent the destruction of the packing material in the trap. The packing material which gave the most reproducible results in the desorption experiments was Tenax GC. For this reason and its stability at the 300°C desorption temperature, the Tenax GC packing material was selected for use in subsequent experiments.

A Tenax trap at -76°C was used to collect the exhaust from a 1975 Model 350 CID Chevrolet engine for the 31 minutes of an FTP. The resulting trap

TABLE 47. THE EFFECT OF COLD TRAPPING AT -196°C ON CARBONYL SULFIDE AND METHYL SULFIDE WITH VARIOUS TRAP SIZES

Trap loop, mℓ	Trap Flow mℓ/min	inj.	Trap Inlet Conc., ppm COS	Trap Inlet Conc., ppm CH_3SCH_3	Trap Inlet Peak Height COS	Trap Inlet Peak Height CH_3SCH_3	Trap Exit Peak Height COS	Trap Exit Peak Height CH_3SCH_3
5.0	81.2	1	1.40	0.71	66.7	5.3	15.8	0.8
5.0	81.2	2	1.40	0.71	66.7	5.3	15.8	0.1
		Avg.	1.40	0.71	66.7	5.3	15.8	0.5
10.0	81.2	1	1.40	0.71	67.8	5.2	16.0	0.0
10.0	81.2	2	1.40	0.71	68.1	5.2	15.2	0.0
		Avg.	1.40	0.71	68.0	5.2	15.6	0.0
15.0	81.2	1	1.40	0.71	67.8	5.2	8.0	0.1
15.0	81.2	2	1.40	0.71	68.1	5.2	10.8	0.1
		Avg.	1.40	0.71	68.0	5.2	9.4	0.1
20.0	81.2	1	1.40	0.71	78.0	5.5	8.0	0.0
20.0	81.2	2	1.40	0.71	78.9	5.5	14.0	0.1
		Avg.	1.40	0.71	78.5	5.5	11.0	0.05

TABLE 48. THE EFFICIENCY OF VARIOUS MATERIALS TRAPPING SULFIDES AT SEVERAL TEMPERATURES

			Gas chromatograph Response-Peak Ht.			
			Before		After	
Inj.	Trap Temp. °C	Trap	COS	CH_3SCH_3	COS	CH_3SCH_3
1	20	Tenax-GC	68.2	4.2	64.5	0.0
2	20	Tenax-GC	69.5	5.3	67.5	0.0
Avg.	20	Tenax-GC	68.9	4.8	66.0	0.0
1	0	Tenax-GC	65.0	4.5	64.5	0.0
2	0	Tenax-GC	63.5	4.7	62.0	0.0
Avg.	0	Tenax-GC	64.3	4.6	63.3	0.0
1	-76	Tenax-GC	64.8	5.0	0.0	0.0
2	-76	Tenax-GC	65.0	5.0	0.0	0.0
Avg.	-76	Tenax-GC	64.9	5.0	0.0	0.0
1	20	Chromosorb 102	68.2	4.2	66.5	0.0
2	20	Chromosorb 102	69.5	5.3	68.0	0.0
Avg.	20	Chromosorb 102	68.9	4.8	67.3	0.0
1	0	Chromosorb 102	64.0	4.9	20.8	0.0
2	0	Chromosorb 102	64.2	4.3	20.0	0.0
Avg.	0	Chromosorb 102	64.1	4.6	20.4	0.0
1	-76	Chromosorb 102	67.2	4.8	0.0	0.0
2	-76	Chromosorb 102	67.2	4.8	0.0	0.0
Avg.	-76	Chromosorb 102	67.2	4.8	0.0	0.0
1	20	Porapak Q	62.0	5.0	63.2	0.0
2	20	Porapak Q	63.6	5.0	62.6	0.0
Avg.	20	Porapak Q	62.8	5.0	62.9	0.0
1	0	Porapak Q	64.0	4.9	35.5	0.0
2	0	Porapak Q	64.2	4.3	45.0	0.0
Avg.	0	Porapak Q	64.1	4.6	40.3	0.0
1	-76	Porapak Q	67.2	4.7	0.0	0.0
2	-76	Porapak Q	67.2	4.5	0.0	0.0
Avg.	-76	Porapak Q	67.2	4.6	0.0	0.0
1	20	Chromosorb T	65.0	4.5	64.8	3.9
2	20	Chromosorb T	63.5	4.5	65.1	4.5
Avg.	20	Chromosorb T	64.3	4.5	65.0	4.2
1	0	Chromosorb T	64.8	5.0	64.0	5.0
2	0	Chromosorb T	65.0	3.9	63.2	5.0
Avg.	0	Chromosorb T	64.9	4.5	63.6	5.0
1	-76	Chromosorb T	64.0	4.8	62.5	3.0
2	-76	Chormosorb T	63.0	4.8	61.0	0.0
Avg.	-76	Chromosorb T	63.5	4.8	61.8	1.5

---

[a] Trap size 2" x 3/8" OD

was thermally desorbed into the GC analysis system. The gas chromatograph trace obtained from the desorption of the trap indicated that a substantial number of sulfur containing compounds were present. The major drawback observed was the exceptionally large sulfur dioxide (SO_2) peak.

The concentration of sulfur dioxide in the dilute exhaust will normally range from 2 to 5 ppm, whereas the other sulfides are present only in the ppb range. The sulfur dioxide is unstable and the proposed method is not designed to quantitatively measure sulfur dioxide. Since sulfur dioxide has no quantitative interest, efforts were directed to determine if techniques are available that would allow sulfur dioxide removal without altering the concentration of other sulfides. A packing material containing sodium bicarbonate ($NaHCO_3$) has been reported to be very effective for this purpose.

Experiments have indicated that hydrogen sulfide (H_2S) was not stable enough to quantify with this procedure. In order to remove the interference from sulfur dioxide and to remove any remaining hydrogen sulfide, the dilute exhaust is passed through a 2" x 3/8" stainless steel cartridge packed with 5 percent sodium bicarbonate on 45/60 mesh Chromosorb P-AW DMC before entering the organic sulfide collecting Tenax GC trap. The sodium bicarbonate trap effectively removes sulfur dioxide at 10 ppm levels and hydrogen sulfide at 1 ppm levels without affecting the organic sulfide concentrations.

Initially, a set of gas chromatograph operating parameters was developed to provide separation of hydrogem sulfide, carbonyl sulfide, sulfur dioxide, methyl mercaptan, methyl sulfide, methyl disulfide, and ethyl sulfide. Since hydrogen sulfide and sulfur dioxide are not of quantitative interest, the original GC operating parameters were modified to shorten the analysis time. The initial GC oven temperature of 0°C was maintained for four minutes and then temperature programmed to 140°C at 32°C/minute. The entire analysis time was about 25 minutes. Operation of 0°C was originally selected to allow separation of hydrogen sulfide and carbonyl sulfide. Since this separation would no longer be necessary, the GC oven parameters were changed to provide a compromise between separation and analysis time. This new programming rate provides for sample injection at 80°C followed by immediate programming to 140°C at 16°C/minute. A typical trace of the organic sulfides is shown in Figure 41.

Several recovery experiments were conducted using the Tenax GC traps. These experiments were designed to determine the recovery of the organic sulfides from the Tenax GC traps. The recovery from these traps was very erratic and was not satisfactory. Initially, it was felt that the lack of reproducibility was due to the technique employed to remove the organic sulfides from the Tenax GC traps. However, the GC analytical column was later found to be suspect. Contact was made with those researchers who originally used the GC parameters to quantitatively measure organic sulfides. Their findings were similar to those experienced at SwRI. When using this column packing near its maximum operating temperature, very erratic results were experienced. After looking into this more thoroughly, it was decided to use a different column packing that would be reproducible and still yield satisfactory separation of the organic sulfides.

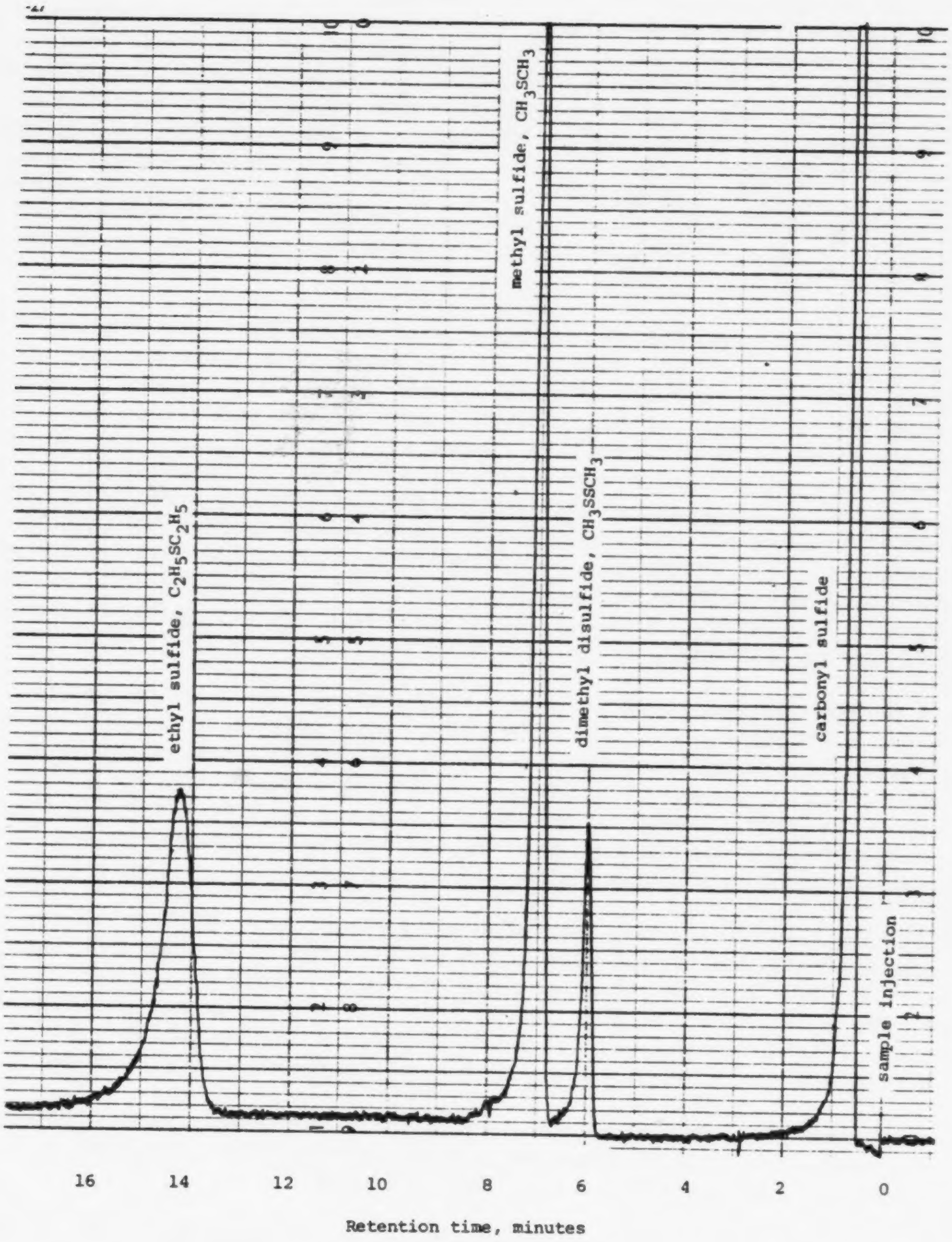


Figure 41. Typical gas chromatograph trace of organic sulfides.

The column packing that was selected was a specially treated Porapak QS. Although this column is reported to be stable at higher temperatures, the separation characteristics are not as good as the Chromosil 310 column. The ethyl sulfide and methyl disulfide elute together. A typical calibration blend from a permeation system is presented in Figure 42. This column was also found to give inconsistent results after repeated use and a different analytical column was sought for use in measuring the organic sulfides. After reviewing the literature and conducting a brief cursory laboratory study, it was found that the column which has the necessary qualifications for the organic sulfide analysis is a 6' x 1/8" TFE Teflon column packed with 60/80 mesh Tenax GC. A typical gas chromatograph trace using the Tenax GC analytical column for the analysis of the four organic sulfide is shown in Figure 43.

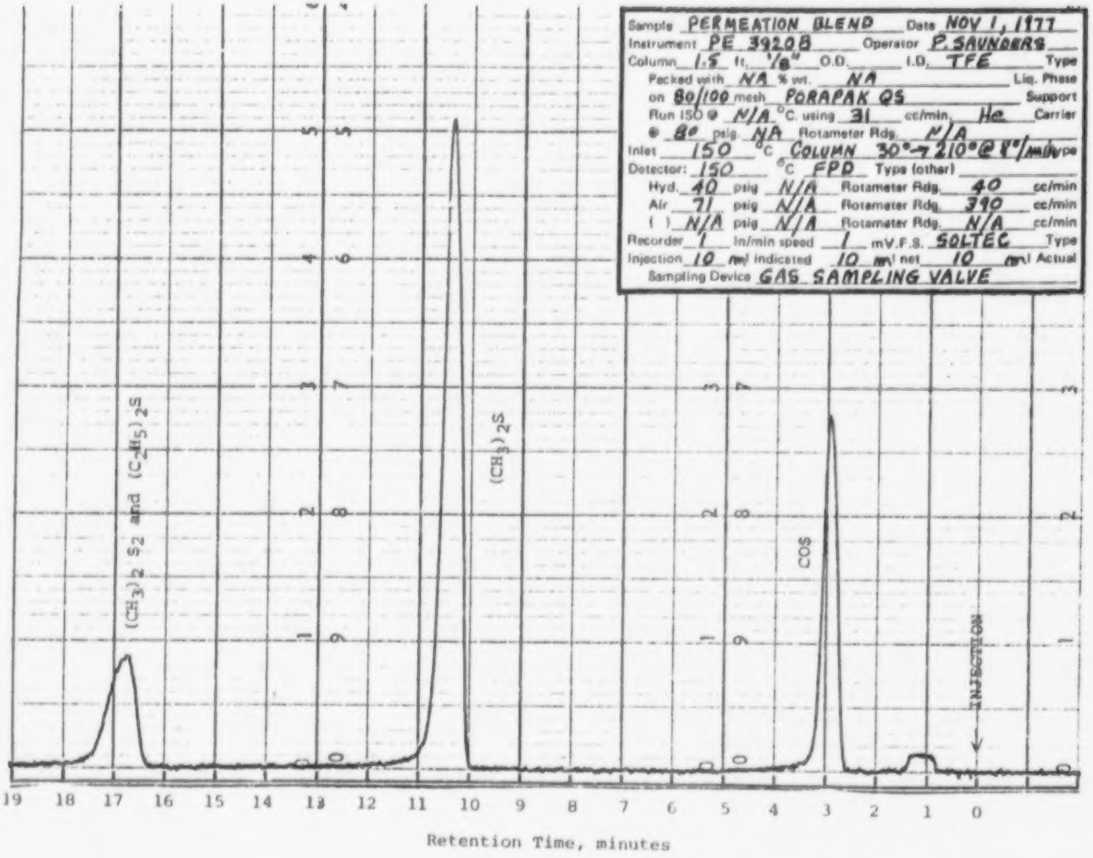
In order to determine the efficiency of the collection of Tenax GC absorbing traps, a secondary dilution of the permeation calibration system was included. The organic sulfides were diluted from a 0.1 - 3 ppm level down to the detection limits of the FPD. A sample of the permeation blend after secondary dilution is presented in Figure 44. As noted, only two of the four peaks are above the detection limits, although all four organic sulfides and the concentrations are listed at their elution time. The concentration of the organic sulfides with Tenax-GC traps appears to have tremendous potential. An example of the permeation calibration blend (with secondary dilution) after being sampled at a flow rate of 45 mℓ/min for 10 minutes is shown in Figure 45. Only the four individual organic sulfides are observed, and no extraneous peaks (reaction products, etc.) are observed.

A system was developed to re-condition the Tenax GC traps by purging the traps with nitrogen at 500 mℓ/min for seven mniutes at 300°C. Several spot checks of traps that had been conditioned under these conditions indicated no trace of organic sulfide carry-over from "used" Tenax-GC traps. The procedure that is used to desorb the organic sulfides from the traps is also very efficient in that no organic sulfides are retained in the trap after the thermal desorption using the GC procedure.

The Tenax GC traps have been found to effectively remove 100 percent of the organic sulfides from a permeation calibration flow at a flow rate of 130 mℓ/min when the trap is maintained at -76°C. Higher flow rates were tried, and a breakthrough into the back-up Tenax-GC trap was observed at a flow rate of 250 mℓ/min. When this occurred, it was decided to return to 130 mℓ/min and use this flow rate as the primary sampling flow rate.

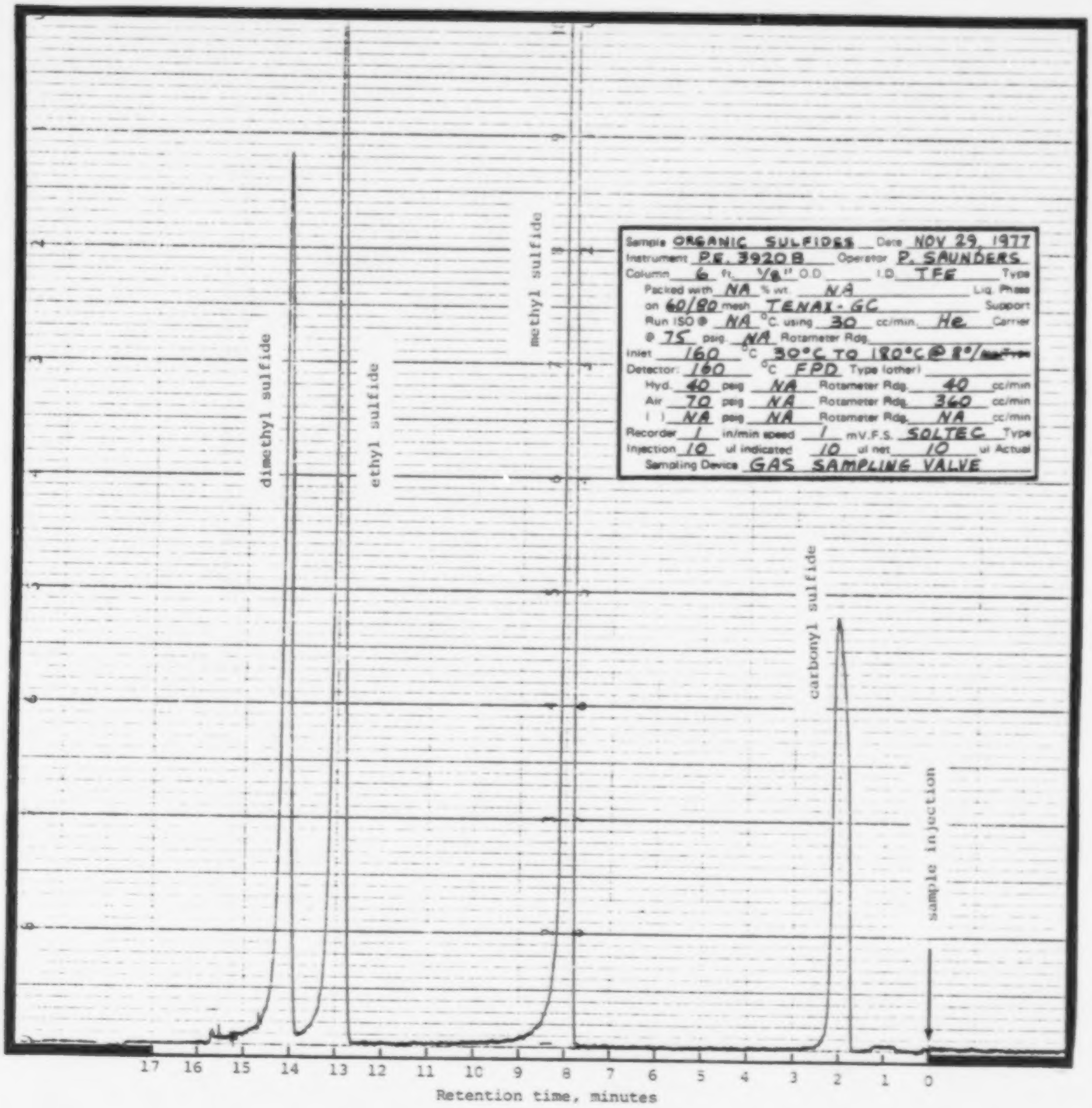
A variety of other trap designs, temperatures, and flow rates may be equally acceptable; but for the purpose of developing a procedure with specific goals, these conditions have been selected.

Problems have been encountered with batch to batch variation in the Tenax-GC which have caused repeatability problems. A procedure has been implemented to validate each Tenax-GC batch prior to sampling as well as each individual trap.



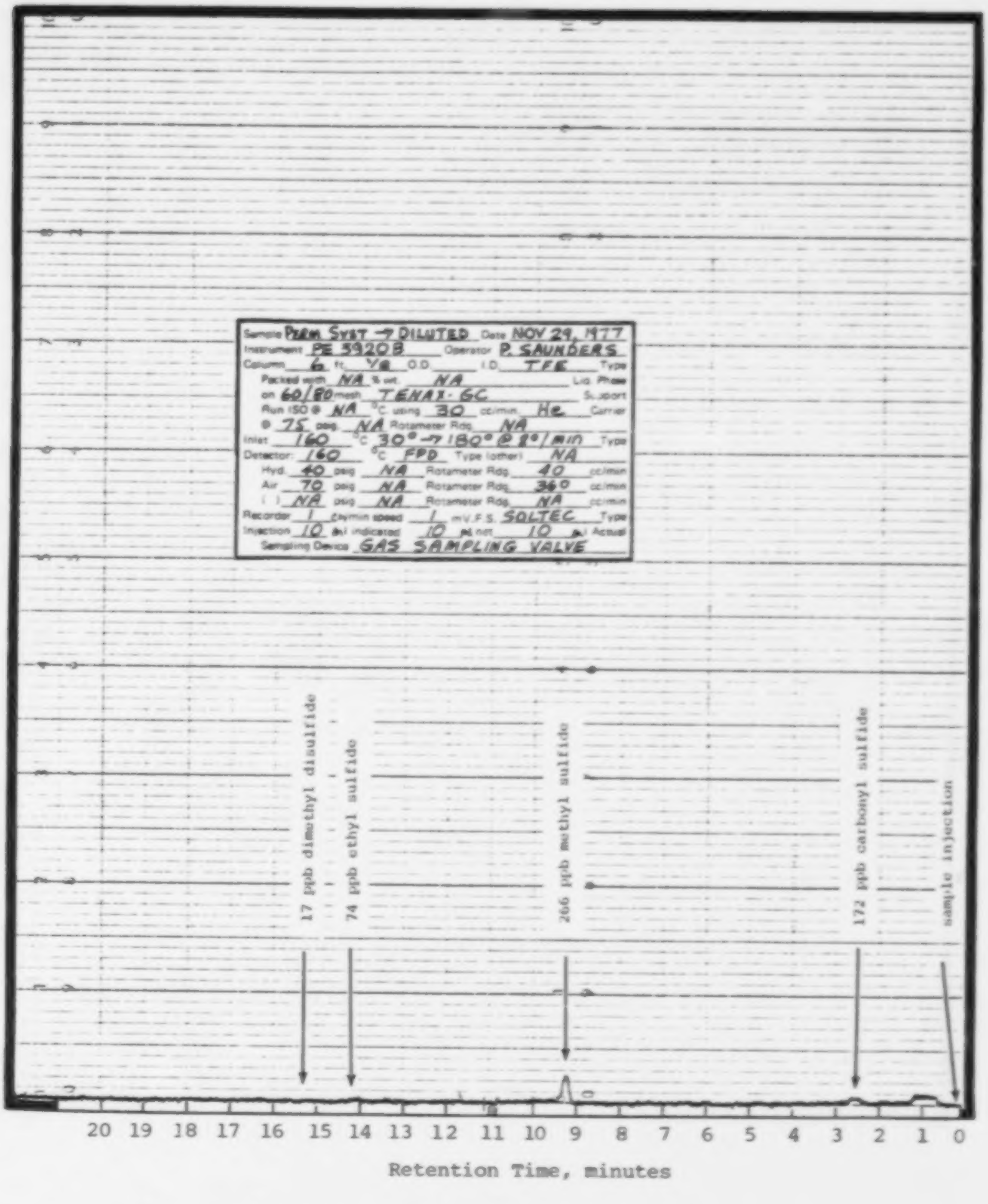
Sample PERMEATION BLEND Date NOV 1, 1977
Instrument PE 3920B Operator P. SAUNDERS
Column 1.5 ft. 1/8" O.D. ____ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 80/100 mesh PORAPAK QS Support
Run ISO @ N/A °C. using 31 cc/min. He Carrier
@ 80 psig. NA Rotameter Rdg. N/A
Inlet 150 °C COLUMN 30°→210° @ 8°/min Type
Detector: 150 °C FPD Type (other) ____
Hyd. 40 psig N/A Rotameter Rdg. 40 cc/min
Air 71 psig N/A Rotameter Rdg. 390 cc/min
( ) N/A psig N/A Rotameter Rdg. N/A cc/min
Recorder 1 in/min speed 1 mV.F.S. SOLTEC Type
Injection 10 ml indicated 10 ml net 10 ml Actual
Sampling Device GAS SAMPLING VALVE

Figure 42. Typical GC separation of organic sulfides on acetone-washed Porapak QS column.



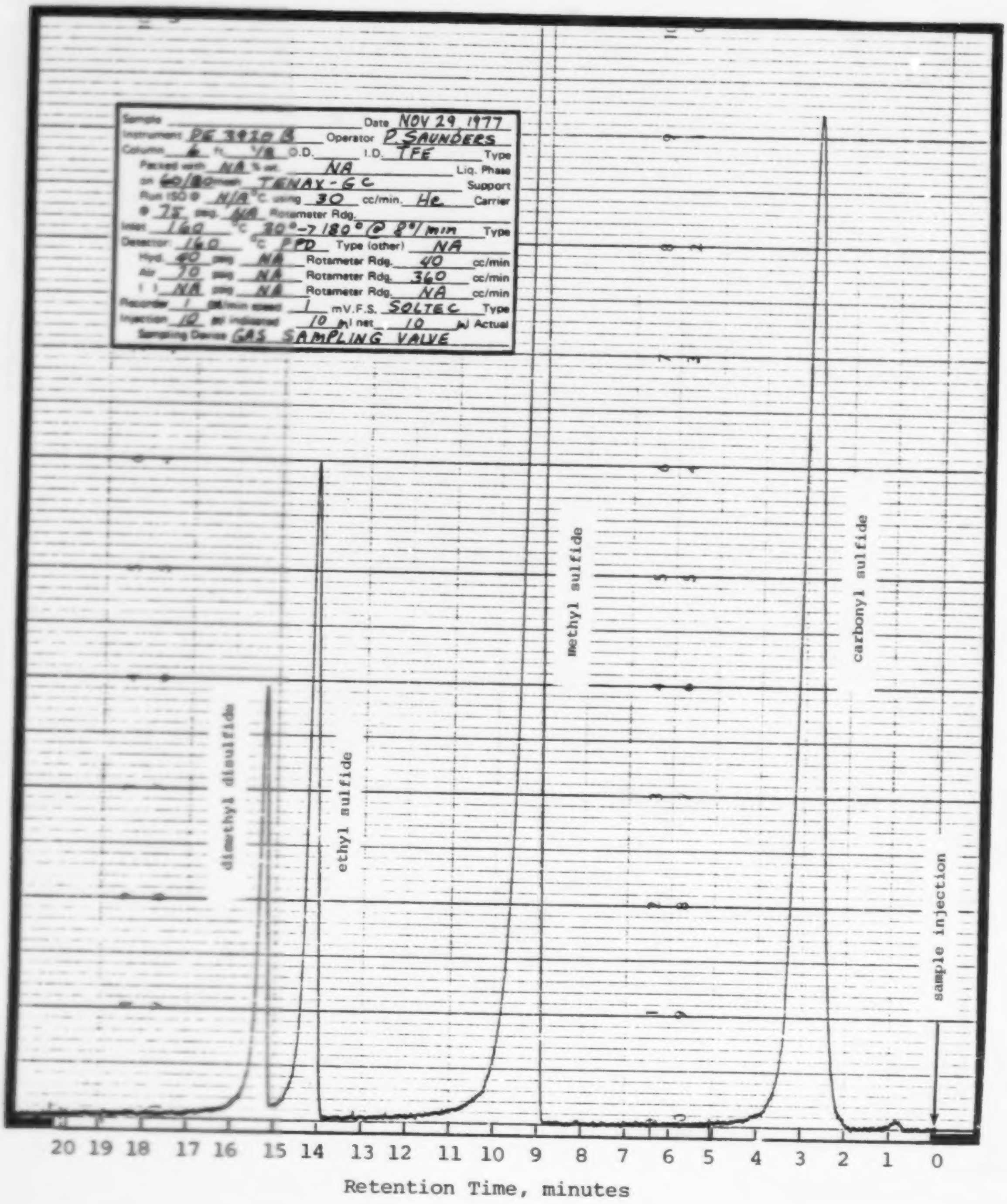
Sample ORGANIC SULFIDES Date NOV 29, 1977
Instrument P.E. 3920 B Operator P. SAUNDERS
Column 6 ft. 1/8" O.D. ____ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ NA °C. using 30 cc/min. He Carrier
@ 75 psig. NA Rotameter Rdg. ____
Inlet 160 °C 30°C TO 180°C @ 8°/[illegible]
Detector: 160 °C FPD Type (other) ____
Hyd. 40 psig NA Rotameter Rdg. 40 cc/min
Air 70 psig NA Rotameter Rdg. 360 cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 in/min speed 1 mV.F.S. SOLTEC Type
Injection 10 ul indicated 10 ul net 10 ul Actual
Sampling Device GAS SAMPLING VALVE

Figure 43. Typical organic sulfide separation with Tenax-GC column.



Sample PERM SYST → DILUTED Date NOV 29, 1977
Instrument PE 3920B Operator P. SAUNDERS
Column 6 ft. 1/8 O.D. ______ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ NA °C using 30 cc/min He Carrier
@ 75 psig NA Rotameter Rdg NA
Inlet 160 °C 30° → 180° @ 8°/min Type
Detector: 160 °C FPD Type (other) NA
Hyd. 40 psig NA Rotameter Rdg 40 cc/min
Air 70 psig NA Rotameter Rdg 360 cc/min
( ) NA psig NA Rotameter Rdg NA cc/min
Recorder 1 cm/min speed 1 mV.F.S. SOLTEC Type
Injection 10 ml indicated 10 ml net 10 ml Actual
Sampling Device GAS SAMPLING VALVE

Figure 44. Organic sulfide permeation blend with secondary dilution, near detection limit of GC FPD system.



Sample ______ Date NOV 29 1977
Instrument PE 3920 B Operator P. SAUNDERS
Column 6 ft. 1/8 O.D. ______ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ N/A °C using 30 cc/min. He Carrier
@ 75 psig NA Rotameter Rdg.
Inlet 160 °C 30°→180° @ 8°/min Type
Detector 160 °C FPD Type (other) NA
Hyd. 40 psig NA Rotameter Rdg. 40 cc/min
Air 70 psig NA Rotameter Rdg. 360 cc/min
I I NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 in/min speed 1 mV.F.S. SOLTEC Type
Injection 10 µl indicated 10 µl net 10 µl Actual
Sampling Device GAS SAMPLING VALVE

Figure 45. Organic sulfide permeation blend with secondary dilution, concentrated on Tenax-GC trap and thermally desorbed into GC FPD system.

The procedure chosen for the analysis of the organic sulfides consists of (1) collecting the organic sulfides on a Tenax GC trap at -76°C; (2) thermally desorbing the organic sulfides from the trap into the GC sampling system; (3) injecting the organic sulfides into the GC; (4) analysis of the organic sulfides with a GC equipped with a sub-ambient oven accessory, a 6' x 1/8" Teflon analytical column packed with Tenax-GC, and a flame photometric detector; (5) and quantifying the results with the use of permeation calibration tubes. A finalized copy of the procedure is included an an appendix to this report.

VALIDATION EXPERIMENTS

Several experiments were carried out to determine the validity of the organic sulfide procedure for the analysis of carbonyl sulfide, methyl sulfide, ethyl sulfide, and methyl disulfide. These experiments included checks for: GC injection variability, linearity of detector response, sample stability in the Tenax traps, trapping efficiency of the Tenax traps, interferences, and test repeatability.

The finalized sampling conditions used to collect the organic sulfides are listed below as is a discussion on their selection. A 2" x 3/8" OD stainless steel trap packed with Tenax-GC is used to collect 99+ percent of the organic sulfides. During sampling, the trap is kept at -76°C in a dry ice-isopropyl alcohol slurry. This temperature is necessary to effectively trap the four organic sulfides from the dilute exhaust sample. Higher temperatures (greater than 0°C) allow carbonyl sulfide to break through the Tenax-GC trap. The other three sulfides can be effectively trapped even at temperatures as high as 20°C. The sample flow rate through the trap is maintained at 130 mℓ/min. At higher flow rates (250 mℓ/min), breakthrough of the organic sulfides occurs. A flip top filter, a Perma Pure Drier, and a trap containing 5 percent sodium bicarbonate on 45/60 mesh Chromosorb P-AW DMCS precede the Tenax GC trap. The flip top filter removes particulate from the gas stream prior to flow through the Perma Pure Drier. If particulate is allowed to enter the Perma Pure Drier, it could posion the drier and prevent it from functioning properly. The Perma Pure Drier removes moisture from the gas stream which could freeze out in the -76°C Tenax-GC trap, thus restricting or stopping flow through the Tenax-GC trap. The 5 percent sodium bicarbonate trap removes sulfur dioxide from the gas stream and prevents it from collecting in the Tenax-GC trap. The sodium bicarbonate trap will remove 10 ppm sulfur dioxide at a sample flow of 130 mℓ/min continuously from dilute exhaust for periods up to 30 minutes. Tenax-GC was chosen as the organic sulfide absorbing material over the other packing materials due to its trapping reproducibility and ability to withstand desorption temperatures.

The Tenax-GC traps can be used many times without replacing the Tenax-GC packing material. There is a large deviation in trapping effiency from batch to batch of the Tenax-GC packing and each batch must be validated prior to sampling. Each trap is conditioned in an oven operating at 325° ± 25°C for one hour with a flow of zero nitrogen (500 mℓ/min) passing through the trap. No carry over of sulfides in the Tenax-GC traps has been found from test to test. This lack of carry over indicates that the desorption process removes 100 percent of the sulfides collected on the trap.

The sample traps must be stored at -76°C before desorption and analysis or carbonyl sulfide will be lost from the traps. The other three sulfides, methyl sulfide, ethyl sulfide, and methyl disulfide, are stable in the traps overnight at room temperature. In most cases, all traps are run between one half hour and three hours after sampling. The traps are capped after sampling with miniature quick connects to prevent condensation of water and other compounds into the trap before analysis. After the traps have been desorbed, they are again capped to prevent contamination before they are used in sample collection again.

To determine the GC injection repeatability for the organic sulfide procedure, a permeation standard containing 1.95 ppm carbonyl sulfide, 3.31 ppm methyl sulfide, 0.84 ppm ethyl sulfide, and 0.20 ppm methyl disulfide was injected into the GC analytical system six consecutive times. The results of this injection repeatability experiment are presented in Table 49. The percent deviation varies from 1 percent for methyl sulfide to 6 percent for methyl disulfide. This deviation appears to increase with decreasing concentration or organic sulfide.

TABLE 49. INJECTION REPEATABILITY FOR THE ORGANIC SULFIDES

Compound	Average GC Peak Area	Standard Deviation	Percent Deviation
Carbonyl Sulfide	29596	420	1.4
Methyl Sulfide	52325	449	0.9
Ethyl Sulfide	11201	254	2.3
Methyl Disulfide	3951	243	6.2

To determine the test-to-test repeatability for the procedure two experiments were carried out. In the first experiment, organic sulfides from a diluted permeation blend were collected on a Tenax-GC trap, desorbed into the injection system, and injected into the analytical gas chromatograph system. This sequence was repeated 5 times using the same Tenax-GC trap and the resulting GC peak areas for each of the organic sulfides were averaged over the 5 tests. Standard deviations and percent deviations were also determined for the organic sulfide GC peak areas. The results of this experiment are presented in Tabel 50. Standard percent deviations ranged from 7 percent of methyl sulfide to 10 percent for carbonyl sulfide and methyl disulfide. The second experiment was identical to the first experiment except that 5 different traps were used to collect the organic sulfides instead of using the same trap 5 times. Table 51 shows the results of this experiment. Standard percent deviations ranged from 13 percent for methyl sulfide to 26 percent for ethyl sulfide.

To determine the linearity of the detector for the concentration ranges of interest, a permeation system containing permeation tubes of all four sulfides was used to generate varying concentrations of the sulfides.

TABLE 50. TRAP REPEATABILITY FOR ORGANIC SULFIDE COLLECTION

	COS Area	Me_2S Area	Et_2S Area	Me_2S_2 Area
Test 1	20241	71938	34417	41346
Test 2	22052	66098	35156	39537
Test 3	20092	74326	38123	41683
Test 4	22343	63777	30508	34147
Test 5	17378	65494	32516	34321
Average	20421	68327	34144	38207
Standard Deviation	±1985	±4548	±2864	±3718
Percent Deviation	9.7%	6.7%	8.4%	9.7%

TABLE 51. TRAP-TO-TRAP REPEATABILITY FOR ORGANIC SULFIDE COLLECTION

	COS Area	Me_2S Area	Et_2S Area	Me_2S_2 Area
Test 1	47590	68995	25716	13839
Test 2	46830	43429	20549	11487
Test 3	44465	66874	17283	10069
Test 4	50590	63440	30144	15901
Test 5	25788	76180	16631	10338
Average	43053	65784	22065	12327
Standard Deviation	±9896	±8332	±5773	±2491
Percent Deviation	23.0%	12.7%	26.2%	20.2%

Figures 46-49 show plots of the GC peak areas vs. the nanograms of each sulfide injected into the GC system. Carbonyl sulfide and ethyl sulfide give linear responses in the 1-200 ng region, methyl sulfide gives a linear response in the 1-120 ng region, and methyl disulfide gives a linear response in the 1-55 ng (higher levels of methyl disulfide were not tried) region. Above 120 ng of methyl sulfide and 200 ng of carbonyl sulfide, the detector is not linear, with the peak area not increasing proportionally with the weight of sulfide injected. The concentration range of sulfides in dilute exhaust which would fall in this linear range with the current sampling technique is 0.1 to 25 ppb. If the concentration of sulfides in the dilute exhaust exceeds a concentration of 25 ppb, a lower sample flow rate will have to be used in order to collect a smaller amount of the sulfides.

Hydrogen sulfide, sulfur dioxide, thiophene, methyl mercaptan, and ethyl mercaptan are sulfur containing compounds that could interfere with the organic sulfide procedure. Sulfur dioxide is present in exhaust at levels which would obscure all other compounds in the GC procedure if it is not removed before it enters the Tenax-GC trap. A 5 percent sodium bicarbonate trap preceding the Tenax-GC trap effectively removes sulfur dioxide from the exhaust without affecting the concentration of the organic sulfides. Hydrogen sulfide at levels of less than one ppm do not pose a problem with the procedure as no breakthrough of hydrogen sulfide into the Tenax-GC trap is detected by the GC-FPD. However, if hydrogen sulfide is present at concentrations of 4 ppm or greater, some hydrogem sulfide is collected on the Tenax-GC trap and is detected by the GC-FPD. If this higher concentration of hydrogen sulfide is present the GC parameters can be modified to prevent hydrogen sulfide from interfering with the analysis of carbonyl sulfide. An oven temperature program which consists of holding the oven temperature at 0°C for 4 minutes and then programming to 140°C at 8°/minute will separate hydrogen sulfide and carbonyl sulfide by nearly two minutes. This program does extend the analysis time for 25 minutes to 45 minutes if the time it takes to recool the GC oven to 0°C is included. Methyl and ethyl mercaptan have yet to be detected in exhaust. If present, the GC operating conditions will separate these compounds from the sulfides of interest. With the present operating conditions, thiophene has a retention time that differs from ethyl sulfide by only seconds. Thiophene and ethyl sulfide have not been effectively speарated by changing the GC operating conditions and therefore, thiophene must be included as a possible source of error in the analysis for ethyl sulfide.

QUALIFICATION EXPERIMENTS

Qualification experiments were carried out using a Mercedes 240D. Hot FTP (23 minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel injection plus vehicle experiments. An aluminum cylinder containing 4-8 ppm of each of the organic sulfides in balance nitrogen was used as the source for the organic sulfides. The cylinder was named by comparing GC peak areas with the GC peak areas of the organic sulfides generated by the permeation system. The flow of organic sulfides into the tunnel was regulated to give a concentration of 5-10 ppb of each of the organic sulfides in the dilution tunnel. Injections of the

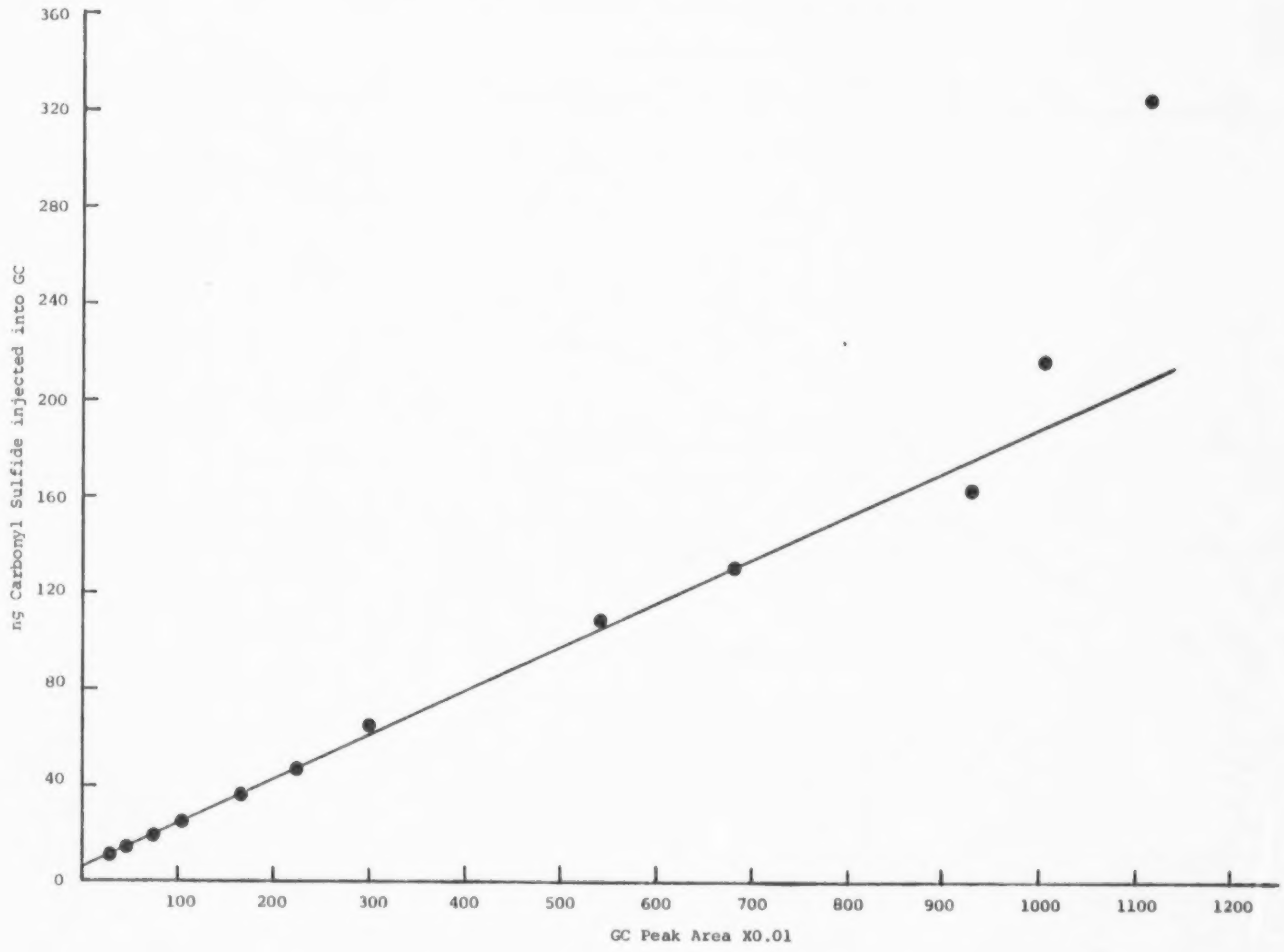


Figure 46. Carbonyl sulfide linearity plot.

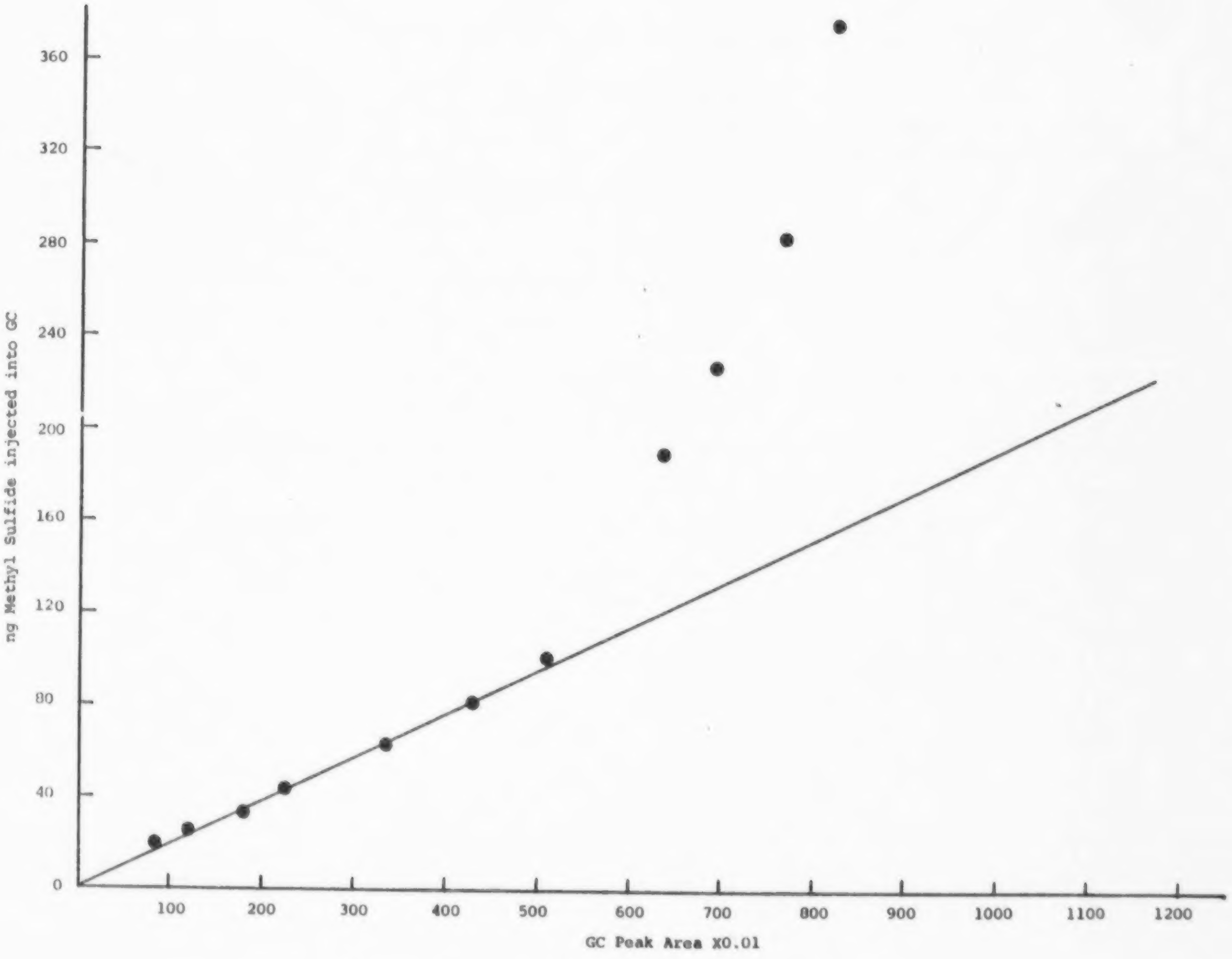


Figure 47. Methyl sulfide linearity plot.

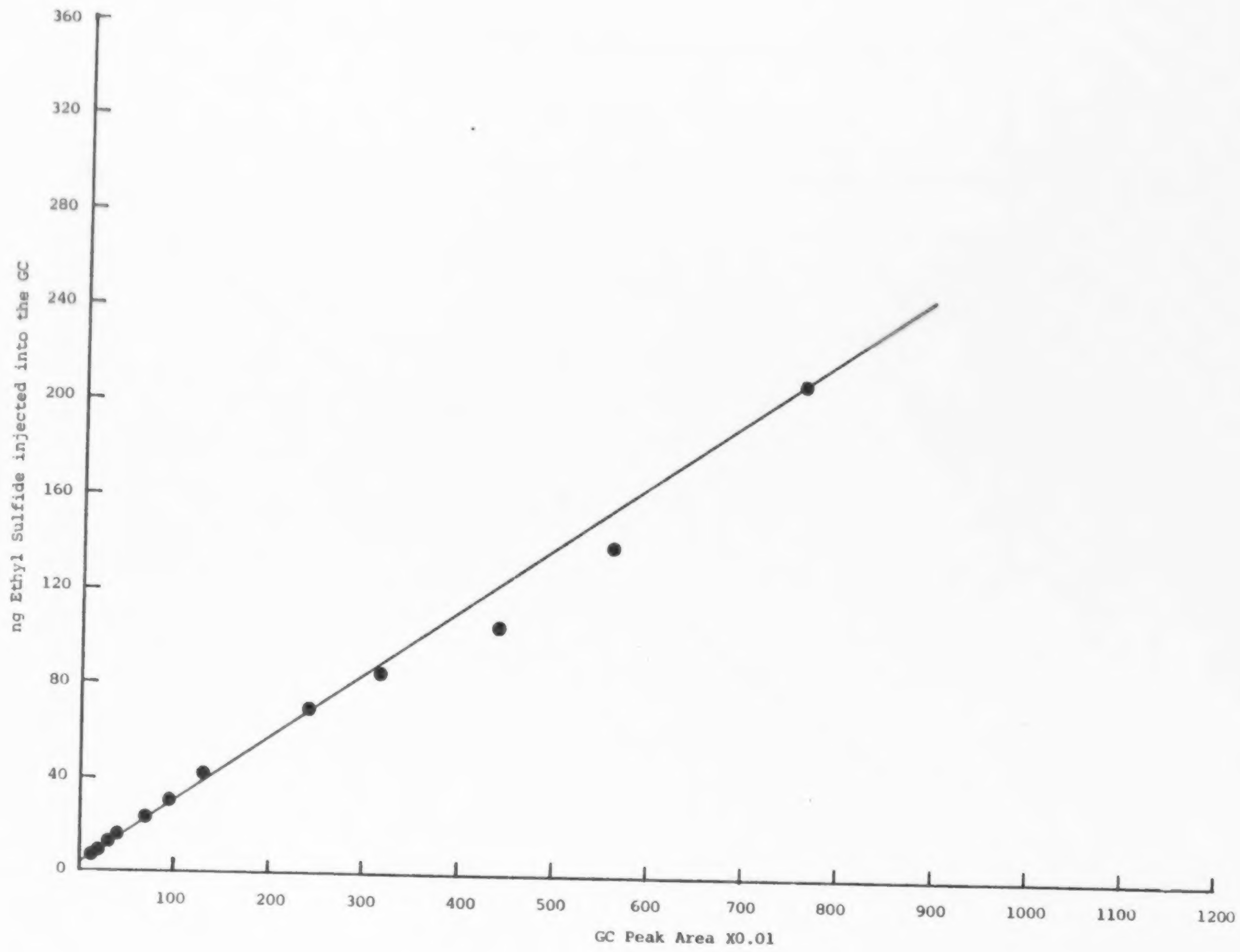


Figure 48. Ethyl sulfide linearity plot.

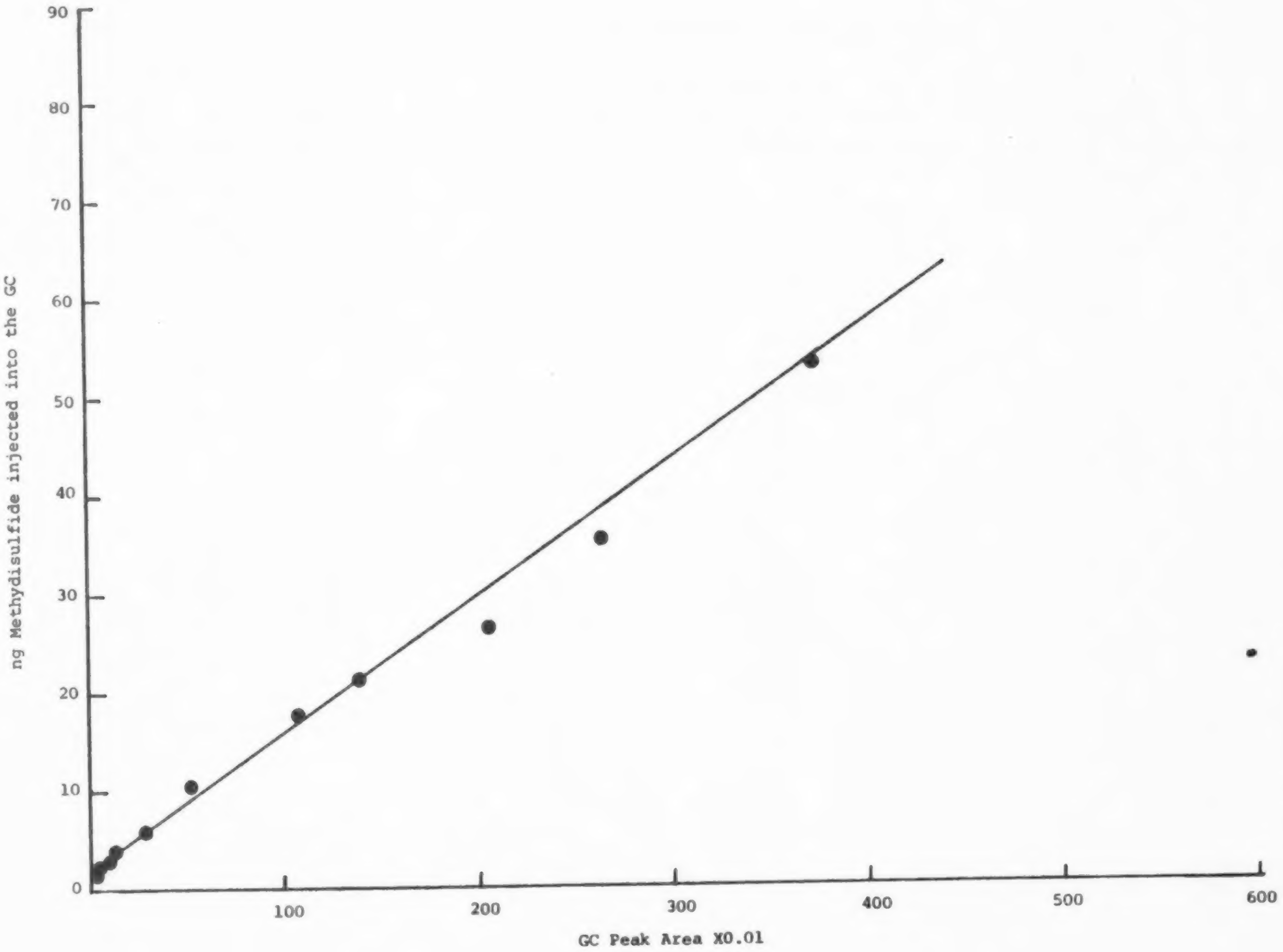


Figure 49. Methyl disulfide linearity plot.

organic sulfides into the tunnel without exhaust gave recoveries that varied from approximately 93 percent for methyl disulfide to 115 percent for ethyl sulfide (Table 52). An interfering peak in the GC analysis for methyl sulfide voided the tunnel recovery experiments for this compound. The percent deviation of the recovery percentages ranged from 23-60 percent. This value is higher than the expected 25% due to the trap-to-trap variations found in the validation experiments. The recovery of the organic sulfides with real exhaust varied from 7 percent for ethyl sulfide to 57 percent for carbonyl sulfide (Table 53). The baseline emissions of carbonyl sulfide and methyl sulfide were erratic and of equal magnitude to the carbonyl sulfide and methyl sulfide injected into the tunnel. This variation of carbonyl sulfide and methyl sulfide from the vehicle, along with tunnel memory for carbonyl sulfide and methyl sulfide and trap-to-trap variations, made the percent recovery calculations very difficult and thus gave the resulting 37 and 55 standard deviations. Baseline emissions for ethyl sulfide, and methyl disulfide were insignificant and did not affect the recovery experiment.

There is little loss of the organic sulfides in the CVS tunnel without exhaust, however a 40 to 90 percent loss with exhaust in the CVS tunnel can be expected. These losses must be taken into account in determining organic sulfide concentrations when using this procedure.

RESULTS AND DISCUSSION

The concentration of organic sulfides can be determined by: 1) trapping the sulfides in a Tenax-GC trap at -76°C, 2) thermally desorbing the sulfides from the Tenax GC trap into the GC injection system, 3) injecting the organic sulfides into the analytical GC system, 4) analyzing the organic sulfides with a gas chromatograph equipped with a flame photometric detector, and 5) quantifying the results by comparison with standards generated by a permeation system. The organic sulfides are effectively caught in the Tenax-GC trap at a flow rate of 130 mℓ/minute. The procedure has a minimum detection limit of approximately 0.2 ppb.

The accuracy of the procedure in the 0.2 to 25 ppb range is on the order of 25 percent due to trap-to-trap repeatability. The FPD gives a linear response for the organic sulfides in the 0.2 to 25 ppb range. If the concentrations of the organic sulfides exceed this range in dilute exhaust, a lower sampling flow rate (less than 130 mℓ/minute) must be used to keep the detector response in the linear range of the detector.

Sulfur dioxide, hydrogen sulfide, and thiophene are possible interferences in the procedure. Sulfur dioxide is removed by the use of a sodium bicarbonate trap, hydrogen sulfide can be separated in the GC system by changing oven parameters; however, thiophene remains an interference to the procedure. The ethyl sulfide concentration is affected by this interference. This is a significant loss of the organic sulfides in the CVS tunnel with exhaust. These losses must be taken into account in determining the concentration of the organic sulfides when using this procedure.

Overall, the organic sulfide procedure should provide a relatively accurate method for determining the concentrations of the organic sulfides in dilute exhaust, and its use is recommended for this project.

TABLE 52. PERCENT RECOVERIES OF THE ORGANIC SULFIDES FROM THE CVS TUNNEL ONLY

	Carbonyl Sulfide (8 ppb) Percent Recovery
	83
	127
	82
	132
	70
Average % Recovery	99%
Standard Deviation	28%

Methyl Sulfide (6 ppb) Percent Recovery
Results voided due to interfering peak in the GC analysis

	Ethyl Sulfide (5 ppb) Percent Recovery
	98
	139
	120
	132
	85
Average % Recovery	115%
Standard Deviation	23%

	Methyl Disulfide (10 ppb) Percent Recovery
	31
	100
	43
	100
	190
Average % Recovery	93%
Standard Deviation	60%

TABLE 53. PERCENT RECOVERIES OF THE ORGANIC SULFIDES FROM THE CVS TUNNEL AND EXHAUST

	Carbonyl Sulfide (8 ppb) Percent Recovery
	20
	42
	119
	52
	54
Average % Recovery	57%
Standard Deviation	37%

	Methyl Sulfide (6 ppb) Percent Recovery
	12
	27
	144
	18
	34
Average % Recovery	47%
Standard Deviation	55%

	Ethyl Sulfide (5 ppb) Percent Recovery
	2
	5
	15
	5
	10
Average % Recovery	7%
Standard Deviation	5%

	Methyl Disulfide (10 ppb) Percent Recovery
	5
	5
	25
	1
	17
Average % Recovery	11%
Standard Deviation	10%

SECTION 11

PHENOL PROCEDURE

LITERATURE SEARCH

Phenols are compounds of the general formula ArOH, where Ar is phenyl or substituted phenyl. Phenols differ from alcohols in having the hydroxyl group, -OH, attached directly to an aromatic ring. Ring substitution by alkyl, hydroxyl or carbonyl groups creates the variety of different phenols possible in automotive exhaust. Phenols generally have high vapor pressures, are colorless and, except for phenol, are insoluble in water. Some of the physical properties of phenols possible in exhaust are shown in Table 54 below.

TABLE 54. PHYSICAL PROPERTIES OF PHENOLS POSSIBLE IN EXHAUST

Phenol	Molecular Weight	Boiling Point, °C	Freezing Point, °C	Density, g/mℓ
Phenol	94.11	182	43	1.0722
Salicylaldehyde	122.13	197	-7	1.1674
m-cresol	108.15	202	12	1.0336
p-cresol	108.15	202	35	1.0178
2,3-xylenol	122.17	218	75	------
3,5-xylenol	122.17	220	68	0.9680
p-ethylphenol	122.17	219	47	------
2-isopropylphenol	136.20	213	15	1.012
2,4,6-trimethylphenol	136.20	221	72	------
2,3,5-trimethylphenol	136.20	230	92	------
2,3,5,6,-tetramethylphenol	150.22	247	118	------
Internal standard- o-chlorophenol	128.56	175	9	1.2634

The slightly acidic nature of phenols ($Ka \approx 10^{-10}$) makes them soluble in aqueous hydroxides yet not acidic enough to be soluble in a bicarbonate solution. This property allows phenols to be separated from non-acidic compounds by collection in base and from organic acids by their insolubility in bicarbonate. The acid base equilibrium that occurs is shown below.

$$\underset{\text{acid}}{\text{Ph-OH}} \underset{H^+}{\overset{^-OH}{\rightleftharpoons}} \underset{\text{salt}}{\text{Ph-O}^-}$$

The purpose of measuring phenols in exhaust is to determine if they are present in sufficient quantities to cause health problems. A number of procedures have been published that are used for determining concentrations of phenols. These include colorimetric or spectrophotometric methods, gas chromatography, liquid chromatography and derivatization with subsequent analysis by gas chromatography. Colorimetric and spectrophotometric methods of phenol analysis (152-154) are primarily used for total phenol measurement. This method is unacceptable because individual phenol concentrations are desired. One liquid chromatography procedure investigated includes the formation of fluorescent dansyl phenol derivatives which are subsequently analyzed by a liquid chromatograph (LC) equipped with a fluorescence detector (155). The procedure is too time consuming to warrant its use. Another liquid chromatograph technique is difficult to set up, is very involved chemically and suffers from interferences in one of the reagents (156). Several procedures were available in which derivatives of phenols were prepared for analysis on a gas chromatograph (GC). In one method, phenols were alkylated over an aluminum phosphate catalyst, acetylated and analyzed on a GC (157). This procedure is very involved and recoveries of phenol are not high. Several methods in which ester (158-160) and ether (161-163) derivatives of phenols are produced were found in the literature search. The production of ether derivatives of phenols and analysis by GC seemed to be a promising method for determining the concentrations of individual phenols. A number of GC methods not involving derivatization were also studied. Some of these listed a variety of columns and GC instrument parameters for phenols analysis (164-173). Phenols can be sampled from exhaust in several ways. Activated carbon filters have been used to absorb phenol from aqueous samples (174) and from air (175). However, a more suitable sampling procedure for dilute exhaust involves collection in a hydroxide solution in impingers. Several authors have suggested this means of removing phenols from exhaust. Collection of phenols in aqueous hydroxide is usually followed by wet chemical workup and analysis by GC. Aqueous phenol samples are treated with a variety of steps including acidification, extraction with an organic solvent, distillation and extractions to remove impurities (176-179).

The procedures that appeared to be the most promising are those using a GC for phenols analysis. Samples can be collected in impingers containing aqueous KOH and workup can be accomplished by forming ether derivatives or by extracting with ether (176).

PROCEDURAL DEVELOPMENT

The procedure chosen for the collection and analysis of phenols required a considerable amount of procedural development. Extraction, analytical and sampling parameters needed to be determined prior to exhaust sample processing.

The first factor investigated, extraction efficiency, was found to depend on a number of variables. Type of solvent, number of solvent extractions, pH of aqueous sample and method of solvent evaporation all affected the extraction efficiency. Two sets of spiked phenol samples were extracted with two solvents, methylene chloride and ethyl ether. Between one and five consecutive extractions were performed and each set of samples using each solvent. The amount and percent of phenol recovered by these extractions is shown in Table 55 and 56. These figures indicate that of the phenol recovered, most or all of it is recovered in the first two solvent extractions. However, four times as much phenol is captured in the second extraction with methylene chloride (8.0 percent) as is captured in the second extraction with ether (1.9 percent). The average recoveries calculated for the two solvents are probably low due to the fact that the averages include cases when only one solvent extraction was performed. Taking into consideration the large difference in extraction efficiencies between the two solvents (67.6 percent with ethyl ether and 49.9 percent with methylene chloride), ether was chosen as the organic solvent for extracting exhaust samples. It is possible that the slightly lower boiling point of ether compared to methylene chloride (34°C vs 40°C) allows it to be boiled off at a lower temperature, thus preventing the evaporation of the lower boiling phenols.

Another factor influencing extraction efficiency was investigated. This was the pH of the phenol spiked aqueous solution. The extraction efficiency was found to be unaffected by the pH of the solution when the pH was neutral or acidic (pH $\leq$ 7). Table 57 lists the amount and percent phenol recovered when the spiked aqueous solution was varied from a pH of one to seven.

TABLE 57. EXTRACTION EFFICIENCY AS A FUNCTION OF pH OF AQUEOUS SOLUTION

pH of Aqueous Solution	Phenol Recovered µg/mℓ	Conc. Spike µg/mℓ	Percent Phenol Recovered
1	34	67	51.8
2	36	67	53.8
3	32	67	47.8
4	28	67	41.8
5	34	67	51.8
6	44	67	65.7
7	32	67	47.8

The fourth factor affecting extraction efficiency that was studied was the means of solvent removal and sample concentration. The method producing the highest phenol recoveries involved a two step process using a Kuderna Danish concentrator heated by a steam bath (45°C) for initial volume reduction and a desiccating chamber modified for dry nitrogen flow for final concentration. Several sample concentrating techniques were tested before it was determined that erratic phenol recoveries occurred when samples were dried solely by heating in a Kuderna concentrator. Phenol recoveries for several samples evaporated to 0, 1/2, 1, 2 and 5 mℓ in the Kuderna concentrator are listed in Table 58. The trend toward increasing phenol recovery with larger final volumes in the Kuderna concentrator is apparent from the data presented in Table 58. Concentrating samples to a desired volume, however, proved to be a difficult task using the Kuderna concentrator. Due to the tapered tip on the concentrator, the solvent level changed rapidly when the volume decreased to 5 mℓ and less. It was necessary, therefore, to

TABLE 55. EXTRACTIONS WITH METHYLENE CHLORIDE

Sample	Phenol Recovered, µg/mℓ Extraction # 1	2	3	4	5	Conc. Spike µg/mℓ	Percent Phenol Recovered Extraction # 1	2	3	4	5	Total Percent Recovered
1	16	2	0	-	-	29	55.2	6.9	0	-	-	62.1
2	24	2	0	-	-	29	82.8	6.9	0	-	-	89.7
3	26	3	0	-	-	29	88.2	10.3	0	-	-	98.5
4	24	-	-	-	-	54	44.4	-	-	-	-	44.4
5	8	-	-	-	-	54	14.8	-	-	-	-	14.8[a]
6	23	-	-	-	-	54	42.6	-	-	-	-	42.6
7	17	-	-	-	-	54	31.5	-	-	-	-	31.5
8	36	-	-	-	-	67	53.7	-	-	-	-	53.7
9	41	-	-	-	-	67	61.2	-	-	-	-	61.2
10	37	-	-	-	-	67	55.2	-	-	-	-	55.2
11	24	-	-	-	-	67	35.8	-	-	-	-	35.8
12	-	9	-	-	-	67	-	13.4[b]	-	-	-	13.4[a]
13	-	24	-	-	-	67	-	35.8[b]	-	-	-	35.8
14	-	37	-	-	-	67	-	55.2[b]	-	-	-	55.2
15	-	-	21	-	-	67	-	-	31.3[b]	-	-	31.3
16	-	-	21	-	-	67	-	-	31.3[b]	-	-	31.3
17	-	-	-	33	-	67	-	-	-	49.2[b]	-	49.2
18	-	-	-	24	-	67	-	-	-	35.8[b]	-	35.8
19	-	-	-	25	-	67	-	-	-	37.3[b]	-	37.3
20	-	-	-	-	32	67	-	-	-	-	47.8[b]	47.8
21	-	-	-	-	33	67	-	-	-	-	49.2[b]	49.2
											Average	49.9

[a] Samples taken inadvertently to near dryness.
[b] All extractions combined to give a total concentration.

TABLE 56. EXTRACTIONS WITH ETHER

	Phenol Recovered, μg/mℓ Extraction #				Conc. Spike	Percent Phenol Recovered Extraction #				Total Percent
Sample	1	2	3	4	μg/mℓ	1	2	3	4	Recovered
1	38	1	0	0	54	70.4	1.9	0	0	72.3
2	23	4	6	3	54	42.6	7.4	11.1	5.6	50.0[a]
3	6	0	0	-	54	11.1	0	0	0	11.1[b]
4	40	0	-	-	54	74.1	0	-	-	74.1
5	31	1	-	-	54	57.4	1.9	-	-	59.3
6	38	0	-	-	54	70.4	0	-	-	70.4
7	42	1	-	-	54	77.8	1.9	-	-	79.7
8	49	-	-	-	54	90.7	-	-	-	90.7
9	45	-	-	-	54	83.3	-	-	-	83.3
10	52	-	-	-	54	96.3	-	-	-	96.3
11	43	-	-	-	54	79.6	-	-	-	79.6
12	18	-	-	-	54	33.3	-	-	-	33.3
13	29	-	-	-	54	53.7	-	-	-	53.7
14	26	-	-	-	54	48.2	-	-	-	48.2
15	30	-	-	-	54	55.6	-	-	-	55.6
									Average	67.6

---

[a] Phenol contamination in all four extractions; total percent recovered represents extractions 1 and 2.

[b] Sample inadvertently taken to near dryness.

TABLE 58. EFFECT OF REDUCING SAMPLE VOLUME BY KUDERNA DANISH CONCENTRATOR ON PHENOL RECOVERY

Evaporative Volume, mℓ	Final Volume mℓ	Phenol Recovered μg/mℓ	Conc. Spike μg/mℓ	Percent Phenol Recovered
5	5	15	21	71.4
2	2	32	52	61.5
1	2	23	52	44.2
1/2	2	20	52	38.5
0	2	14	52	26.9

find another method of sample concentration that did not require constant attention. The second drying method attempted involved the use of the Kuderna concentrator and a tray of heated sand equipped with a dry nitrogen outlet. The samples were concentrated to 5 mℓ in the Kuderna concentrator, transferred to a 10 mℓ beaker and then further concentrated with a stream of dry nitrogen (while being gently heated with the sand). This method was unsuccessful due to water condensation on the beaker and nitrogen blowing sand into the beaker. The warm sand tray was abandoned as a means of drying phenol samples in favor of a desiccating chamber modified for the flow of dry nitrogen. The samples were concentrated to 5 mℓ in the Kuderna concentrator and transferred to 10 mℓ beakers as was done previously. The samples were then concentrated to approximately 1 mℓ in the desiccating chamber by directing dry nitrogen into the beakers with a gas manifold. Water condensation was no longer a problem because the molecular sieve/silica gel absorbant in the chamber absorbed any moisture that was present. The drying process could also be easily observed through the glass window and stopped when necessary. This last procedure was the one adopted for the concentration of extracted phenol samples in ether due to its simplicity and lack of interferences.

A second parameter (in addition to extraction efficiency) affecting the workup of phenol exhaust samples was investigated. This factor was chemical interferences to phenol recovery. The source of interferences could be contaminants in the various reagents used in sample collection or extraction or interfering exhaust compounds trapped in hydroxide solution along with the phenols. Several blank extractions were performed with methylene chloride and with ether using all solutions that would normally be used for exhaust sample extraction. None of the samples produced measurable levels of phenols. Possible interfering compounds in exhaust that may be absorbed into the scrubber solution, 1 N KOH, are neutral hydrocarbons and organic acids. A set of tests were performed in which 1 N KOH samples spiked with diesel fuel were extracted in several ways. In the first experiment 1 μℓ of diesel fuel was added to acidified 1 N KOH spiked with phenol and the resulting sample was extracted and analyzed. The second test was conducted similarly to the first except that a cyclohexane extraction was performed on the basic solution to remove neutral hydrocarbons before acidification, extraction and analysis. In the third extraction an acidified 1 N KOH solution was spiked with 1 μℓ of diesel fuel (no phenol), extracted and analyzed.

Several regular extractions were also performed on phenol spiked 1 N KOH samples. The results, shown in Table 59 indicate that diesel fuel does not interfere with phenol recovery when present by itself. However, when both phenol and diesel fuel were present, an approximate 16 percent phenol loss occurred. The loss increased to 30 percent when a cyclohexane extraction was performed to remove diesel fuel. Additional extractions were performed on an actual exhaust sample and on phenol spiked 1 N KOH samples to determine the validity of the data obtained for Table 59. One half of an aqueous exhaust sample was acidified, extracted and analyzed. The remaining half of sample was first extracted with ethyl ether to remove netural hydrocarbons. Then the ether was extracted with 0.5 N NaOH to recover any phenol extracted into the ether. The aqueous portions were combined, acidified, extracted and analyzed the same as the first half. The same amount of phenol was recovered from each half of the sample. Also, neither of the sample halves contained compounds that could interfere with the GC analysis of the phenols. See Table 60. Apparently, either no neutral hydrocarbons survive the normal extraction process or else these compounds are eluted under the solvent peak during GC analysis of the phenol sample. The two 1 N KOH samples spiked with phenol that were extracted for neutral hydrocarbon removal had an average phenol recovery 70 percent less than samples spiked and extracted normally. The data obtained from the experiments conducted to determine neutral hydrocarbon interference produced conflicting results. However, since the exhaust sample showed no evidence of interference from such compounds, it was decided not to incorporate a neutral compound removal step into the procedure.

TABLE 59. EFFECT OF DIESEL FUEL ON RECOVERY OF PHENOL

Sample Extracted (in 1 N KOH)	Phenol Recovered μg/mℓ	Phenol Added μg/mℓ	Percent Phenol Recovered
1. Phenol + diesel fuel	21	30	70.0
2. Phenol + diesel fuel + cyclohexane extraction	16	29	55.2
3. Diesel fuel	0	0	----
4. Phenol	24	28	85.7

Interference to phenol recovery or analysis due to the presence of organic acids was also studied. The modification to the procedure for removal of organic acids included an additional $NaHCO_3$ extraction of the ether containing the phenols and a back extraction of the aqueous $NaHCO_3$ layer with ether. Organic acids are more soluble in an alkaline aqueous solution than in ether. However, phenols being acidic, tend to be drawn into the $NaHCO_3$ layer along with the organic acids. The back extraction with ether was to recover phenols that may have been extracted into $NaHCO_3$. Two phenol spiked 1 N KOH samples were extracted following the modified procedure to determine the presence of organic acids. The phenol level of the phenol spiked 1 N KOH samples averaged 567 percent higher than samples extracted normally. Half of each exhaust sample was extracted normally and half was

TABLE 60. INTERFERENCES TO PHENOL RECOVERY OR ANALYSIS

Phenol Spiked 1 N KOH Samples	Phenol Recovered μg/mℓ	Percent Phenol Recovered[a]
Normal extractions	3	100
Hydrocarbon modified samples	1	33
Organic acid modified samples	17	567

---

[a] Percent phenol recovered is relative to the samples extracted normally.

Exhaust Sample	Extraction Method	Phenol Recovered μg/mℓ	Percent Difference Between Halves
1	1/2 normal	1	0
	1/2 HC modified	1	
2	1/2 normal	35	0
	1/2 org. acid modified	35	
3	1/2 normal	41	15
	1/2 org. acid modified	35	

extracted with the modification to the procedure. The concentration of phenol recovered from each sample half of the first exhaust sample was the same. The second exhaust sample did not agree as closely as the first, though, probably due to an error in the extraction process. The sample half extracted for removal of organic acids yielded 15 percent less phenol than the sample half extracted normally. Since neither exhaust sample showed any evidence of interference from organic acids, the procedure was not modified for removal of organic acids. The results of the organic acid interference tests are shown in Table 60.

The next set of parameters that needed to be determined were those governing the analytical portion of the phenol procedure. The instrument parameters for the gas chormatograph (GC) and an analytical column for separation of phenols needed to be selected. Also, phenols recovered from exhaust needed to be identified and the response factors calculated. Several different columns were installed in a Perkin-Elmer 3920 GC equipped with a flame ionization detector (FID). These included an SE-30 WCOT glass capillary column, a 10 percent OV-101 on 100/120 mesh Gas-Chrom Q Teflon column, a 20 percent DEGS on 80/100 mesh Chromosorb W-HP Teflon column and a Teflon column packed with 10 percent OS 138/H_3PO_4/SP-1200 on 100/120 mesh Chromosorb W AW. The last column packed with 10 percent OS 138 provided the best separation of phenols of all columns tested. A variety of temperature programming sequences were experimented with on the GC. The most efficient separation of solvent peak from phenols plus an analysis time of less than an hour were obtained with a temperature program of 4°/min from 70°C to 170°C. The temperature is initially held isothermally for two minutes at 70°C. The injector and interface temperature are maintained at 200°C.

Phenols in exhaust samples were identified by comparing the retention times to individual standards and standard blends. The concentrations of phenols in the blend used as the external standard need to be close to the phenols concentrations found in exhuast due to the fact that both retention times and response factors vary with concentration. Response factors, which correct for the different responses of each phenol to the FID, are calculated from the concentration and counts of each phenol in the external standard relative to o-chlorophenol (also in the external standard). The concentrations of phenols in exhaust samples are computed by comparing the area of each phenol to the appropriate response factor and to the area and concentration of the internal standard, o-chlorophenol. Using an external and an internal standard proved to be the easiest and most accurate method of calculating phenol concentrations in exhaust.

The last set of parameters that needed to be determined as part of the procedural development were those relating to the sampling of exhaust for phenols. The procedure chosen for phenols analysis required that phenols be present in an aqueous solution at the start of the extraction process. Since phenols are acidic and therefore soluble in base, it was decided that dilute exhaust would be bubbled through 1 N KOH in glass impingers. The phenols collected in this manner could be extracted directly. The number of impingers and the flowrate of dilute exhaust passing through the impingers that would trap the most phenols needed to be determined. Initially, experiments were conducted with three tapered tip impingers connected in series. Each impinger contained 25 mℓ of 1 N KOH chilled to ice bath temperature. Exhaust was pumped through the impingers at 4 ℓ/min. The samples thus obtained were extracted and analyzed for phenols, however, no phenols were found. In an effort to trap more phenols dilute exhaust was passed through larger Greenburg-Smith impingers at a higher flowrate (0.7-0.8 ft^3/min). Each of the three impingers contained 200 mℓ of 1 N KOH instead of 25 mℓ. Measurable levels of phenols were extracted from exhaust under the latter conditions. Additional tests regarding the choice of sampling parameters is shown in the Validation Experiments section.

VALIDATION EXPERIMENTS

Several experiments were performed to show that the phenol procedure is a valid method for processing exhaust samples containing phenols. The sampling parameters providing the best trapping efficiency were determined. Dilute exhaust is allowed to flow at 0.7-0.8 ft^3/min through two Greenburg-Smith impingers in series. Each impinger contains 200 mℓ of 1 N KOH chilled to ice bath temperatures (0-5°C). From the results shown in Tables 55 and 56 it is obvious that no phenol is captured in bubblers two and three. However, several other phenols (salicylaldehyde, m-cresol, p-cresol, 2,3-xylenol, 3,5-xylenol, etc.) are found in small quantities in the second impinger. For this reason, two bubblers are used to collect phenols. Before passing through the impingers the dilute exhaust flows through a heated sample line (375°F), a Pallflex filter and another sample line heated to 175°F. Tests were conducted with and wirhout a filter. The sample line without a filter was heated to 175°F from the CVS to the impingers. Results from the qualification tests in Tables 62 and 63 show that from 4% to 60% more phenol is recovered from filtered exhaust than from unfiltered exhaust. For this reason exhaust is filtered before sampling for phenols.

The next set of parameters that needed to be determined were those that would give the highest recovery of phenols from the extraction process. It was found that two ether extractions of the contents of impinger one, and one ether extraction of the contents of impinger two gave good recoveries. Also, better results were obtained when the final drying step was done with dry nitrogen instead of with heat. Extraction efficiency of the phenols procedure is approximately 68%.

Two experiments were performed to validate the analytical protion of the phenol procedure. The first involved the analysis of phenol stnadards in the concentration ranges expected in exhaust samples. Calibration curves were drawn from the data and they are shown in Figures 50-56. The linearity ranges of the internal standard and of the phenols found in exhaust vary between 0-50 μg/mℓ and 0-200 μg/mℓ. The range for each phenol is listed in Table 61 below. The ocncentrations of phenol recovered from exhaust are well within the linearity range of each phenol.

TABLE 61. LINEARITY RANGES OF INTERNAL STANDARD AND OF PHENOLS IN EXHAUST

Phenol	Linearity Range (μg/mℓ)
o-chlorophenol	0-120
phenol	0-50
salicylaldehyde	0-120
m-cresol and p-cresol	0-80
p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol and 2,4,6-trimethylphenol	0-200
2,3,5-trimethylphenol	0-100
2,3,5,6,-tetramethylphenol	0-120

Injection variability was studied as another validation test for the phenols procedure. A 12.2 μg/mℓ phenol standard in methylene chloride was injected five consecutive times. The area of each injection is shown in Table 62. The standard deviation is 107 and the percent variations is 2.20% for the five injections.

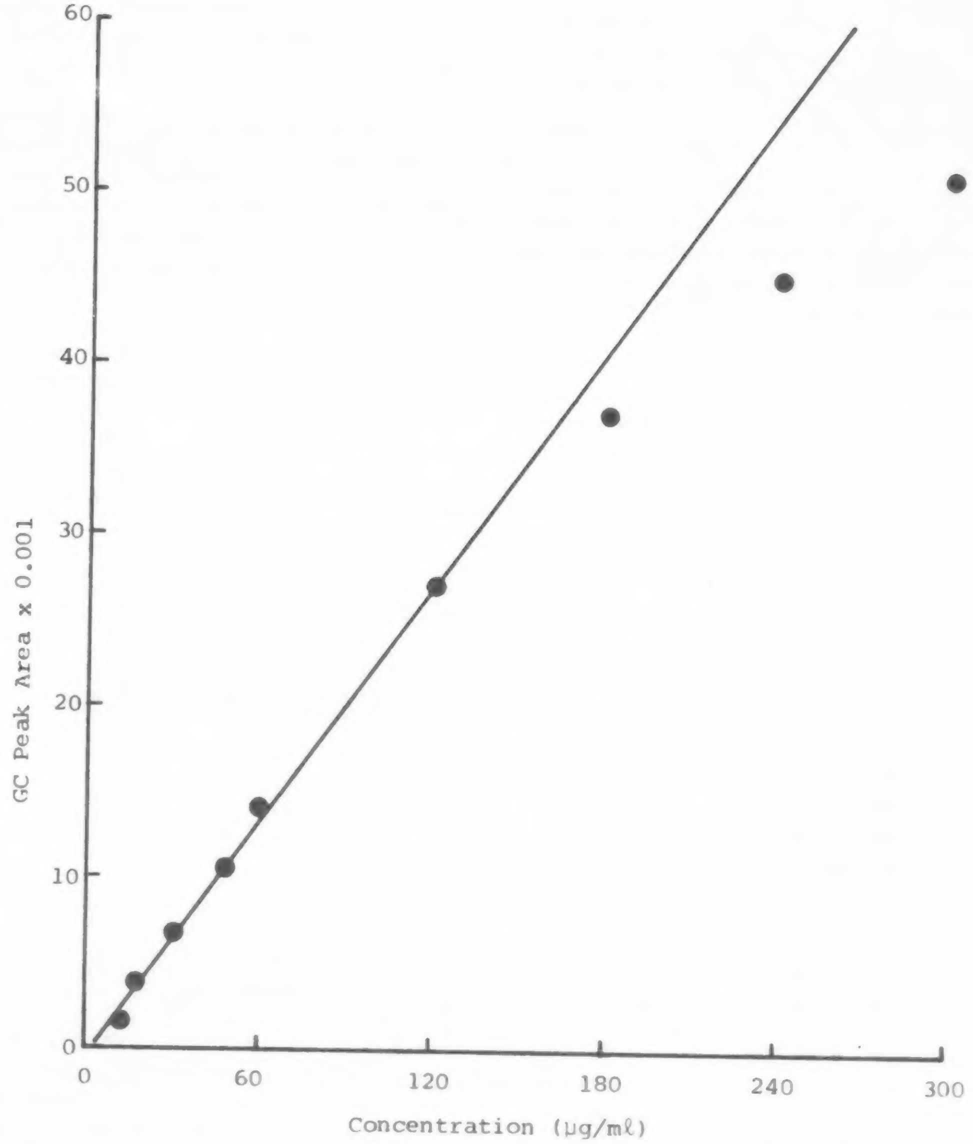


Figure 50. Linearity of o-chlorophenol GC response.

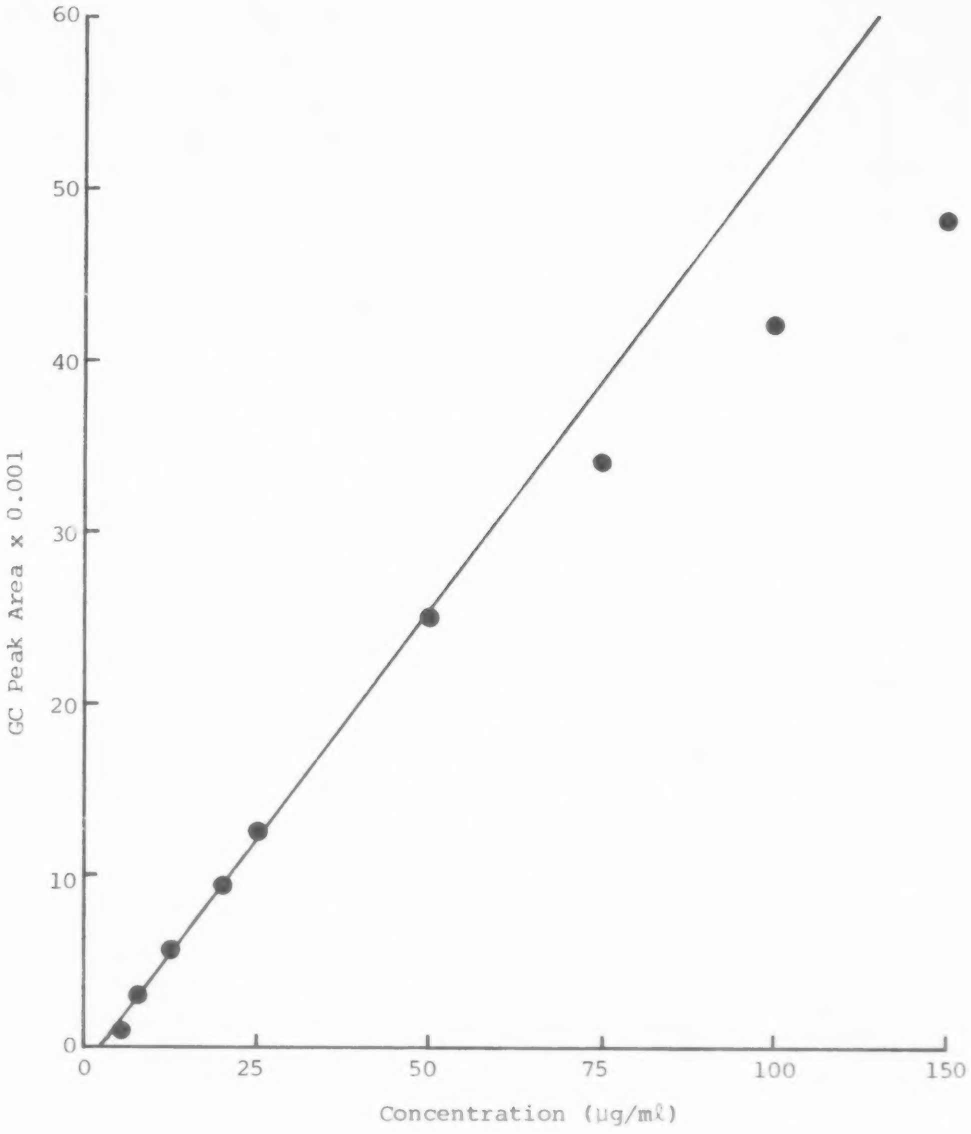


Figure 51. Linearity of phenol GC response.

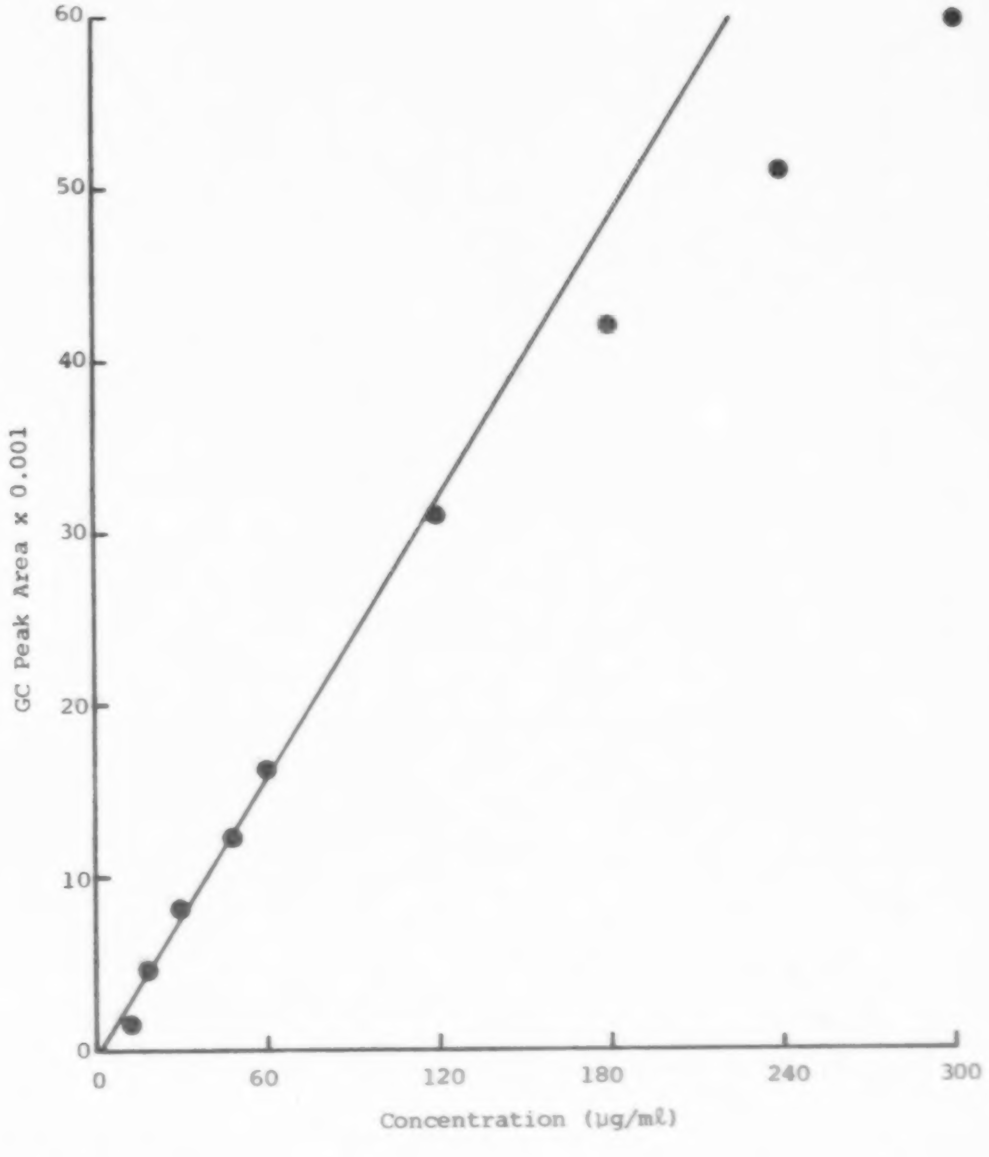


Figure 52. Linearity of salicylaldehyde GC response.

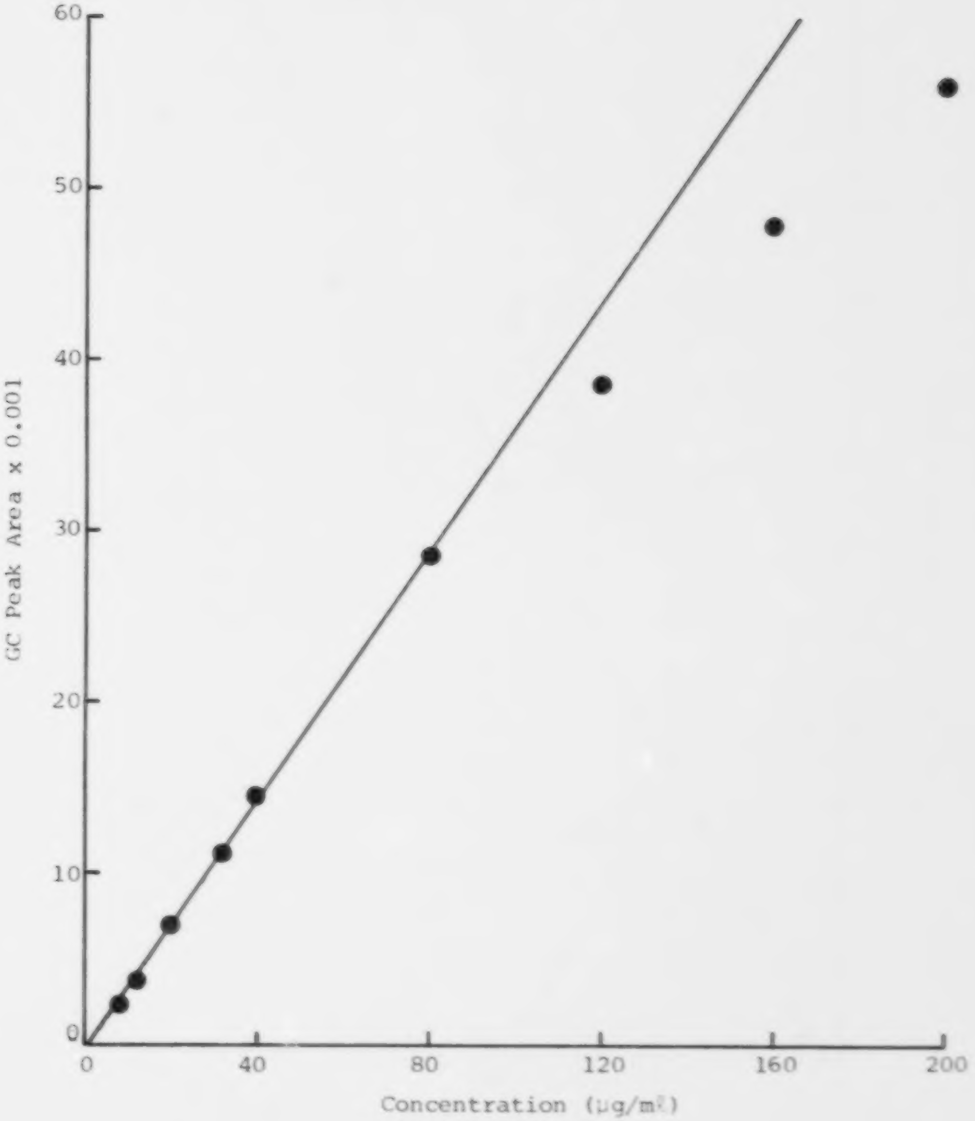


Figure 53. Linearity of m-cresol and p-cresol GC response.

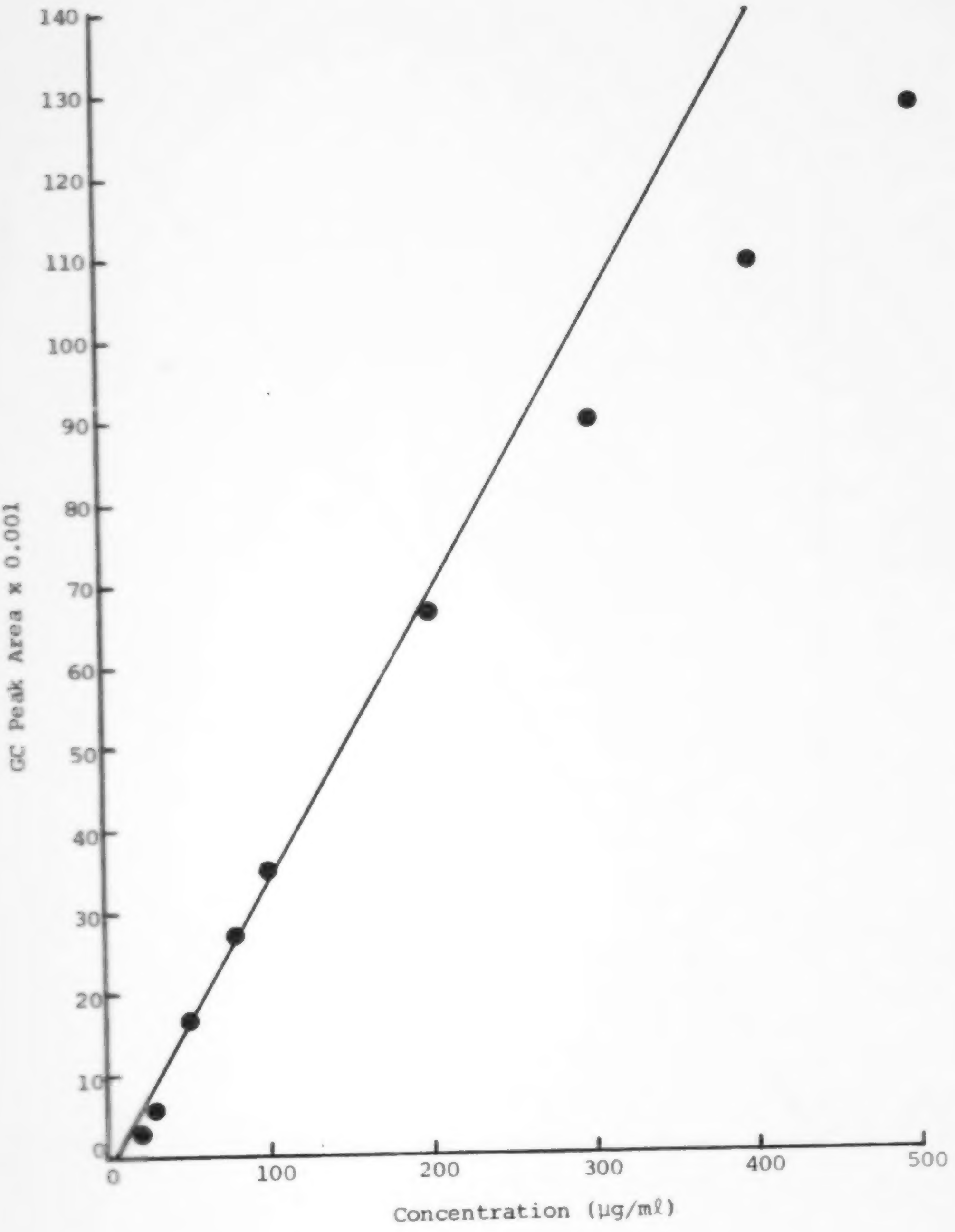


Figure 54. Linearity of p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol and 2,4,6 -trimethylphenol GC response.

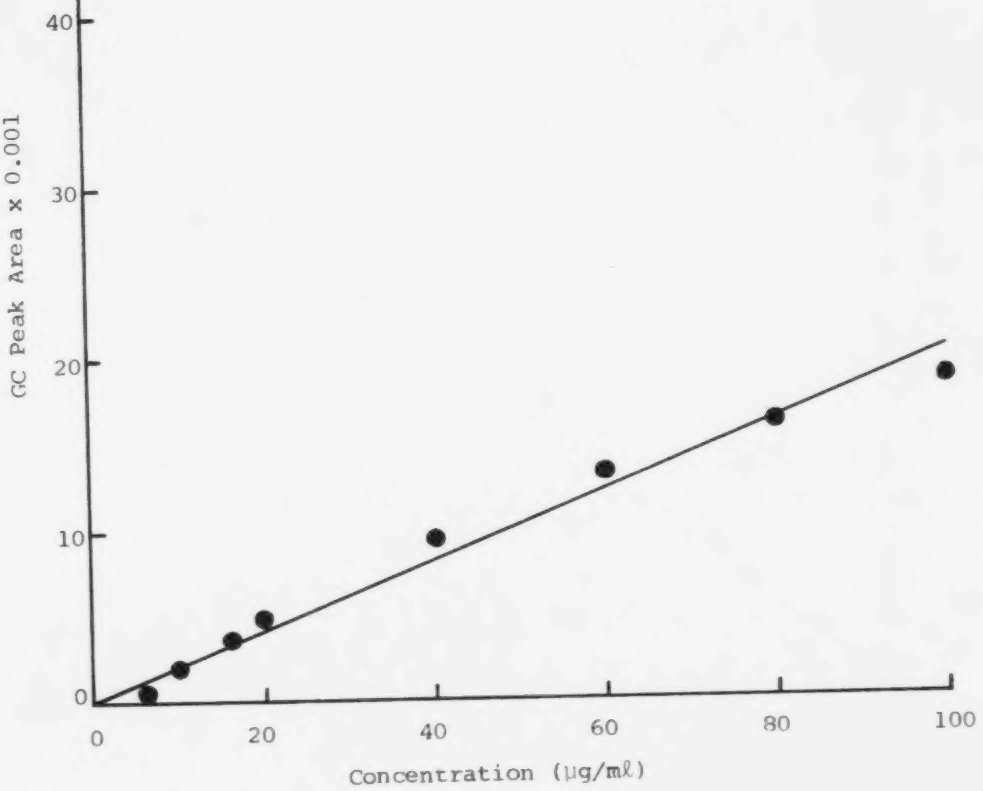


Figure 55. Linearity of 2,3,5-trimethylphenol GC response.

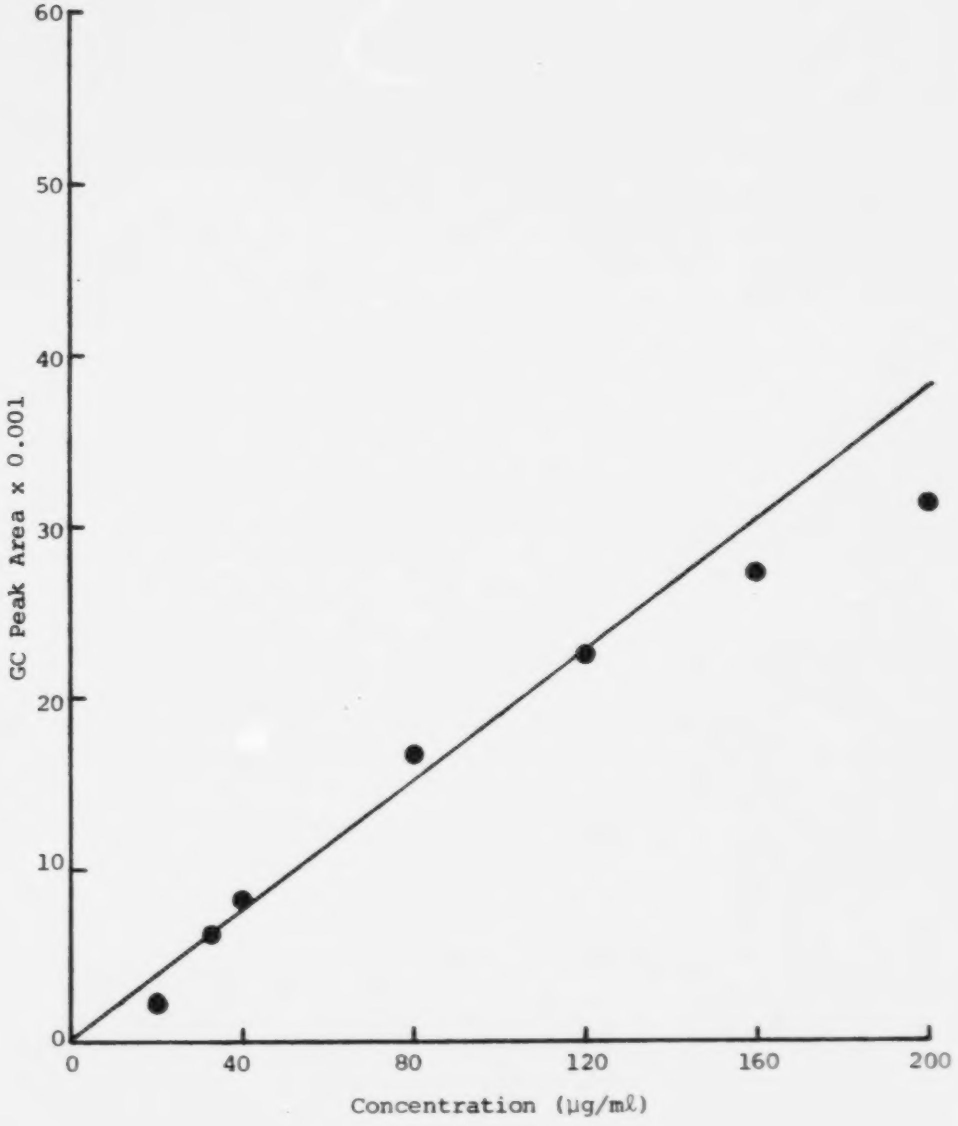


Figure 56. Linearity of 2,3,5,6-tetramethylphenol GC response.

TABLE 62. INJECTION VARIABILITY OF PHENOL

Sample	Area
1	4753
2	4815
3	4921
4	5033
5	4855
Average	4875
Standard Deviation	107
Percent Variation	22.0%

QUALIFICATION

The phenol procedure was qualified by injection of an aqueous phenol solution into the exhaust of a Mercedes 240D diesel during three successive FTPh driving cycles. The percent recoveries from the tests represent the amount of phenol that is expected to survive the trip through the dilution tunnel to the sampling impingers. The test sequence consisted of FTPh driving cycles with ten minute soaks in between. Base line phenol emission levels were measured for three consecutive FTPh driving cycles and during three additional FTPh driving cycles phenol was injected into the exhaust. Two sets of impingers sampled dilute exhaust during each test. The sample line leading to the first set was heated to 175°F and no filter was used. The second sample line was heated to 375°F up to a Pallflex filter and 175°F from the filter to the second set of impingers. The average results from the three baseline emission tests showed that filtered exhaust produced a higher phenol concentration (24 $\mu g/m^3$) than unfiltered exhaust (12 $\mu g/m^3$). The data is found in Table 63 below.

TABLE 63. BASELINE PHENOL EMISSION LEVELS FROM
MERCEDES 240D DIESEL

	$\mu g/m^3$ Phenol		
Test	Unfiltered	Filtered	Difference
1	10	29	19
2	10	--	--
3	15	19	4
Avg	12	24	

The difference between filtered and unfiltered exhaust was also apparent in the results from the injection of phenol into exhaust. The data in Table 64 shows that the filtered exhaust yielded 60 percent and 17 percent more phenol than unfiltered exhaust. No phenol was recovered from the filtered line second phenol injection. This was probably due to sample loss during the

TABLE 64. PERCENT RECOVERIES FROM INJECTION OF PHENOL INTO EXHAUST OF MERCEDES 240D DIESEL

	Unfiltered	Filtered	Difference
First Phenol Injection	52.4	112.7	60.3
Second Phenol Injection	57.7	-----	----
Third Phenol Injection	76.4	93.7	17.3
Average	62.2	103.2	

extraction procedure. A gradual trend towards increasing phenol recoveries appears to occur with samples that flowed through the unfiltered sample line. This may be due to phenols being initially absorbed onto particulate coating the sample line. The particulate removes phenol from the gas stream until it is saturated. Gradually less phenol is absorbed and therefore, more is recovered in the impingers. What appears to be a trend, however, may also be the expected variability in recoveries. The greatest difference in unfiltered recoveries is 24 percent and in filtered recoveries it is 19 percent. The average phenol recovery of unfiltered samples is 62.2 percent and the average phenol recovery of filtered sample is 103.2 percent. Assuming all phenols in exhaust can be removed with similar efficiencies, quantitative recoveries of phenols in exhaust diluted by the CVS can be expected.

The injection of phenol into the exhaust of the Mercedes was accomplished by means of a Baird atomizer attached to an opening on the CVS tunnel. An aqueous phenol solution (0.7 g/mℓ)was dripped into the funnel of the atomizer from a 50 mℓ buret. Air pressure applied through the side arm of the atomizer sprayed the phenol solution into the tunnel where it mixed with exhaust. Any solution that was not dispersed into the tunnel was captured in an Erlenmeyer flask containing the mister. This remaining portion of phenol solution was extracted and analyzed as usual. The amount of phenol injected was calculated by subtracting the micrograms of phenol in the remaining phenol solution from the micrograms delivered from the buret. Percent recoveries were computed by comparing the amount of phenol recovered to the amount injected.

RESULTS AND CONCLUSIONS

The method chosen for measuring phenols in dilute exhaust involves collection in aqueous KOH, extraction with ether and analysis on a GC equipped with a flame ionization detector. Dilute exhaust is bubbled at 0.8 ft^3/min through two Greenburg-Smith impingers each containing 200 mℓ of 1 N KOH chilled to ice bath temperatures. The exhaust is heated to 375°F and is filtered through a Pallflex filter to remove particulate. The phenol samples are acidified, extracted two consecutive times with ethyl ether and concentrated. The extracts from impingers one and two are combined, further concentrated and spiked with the internal standard, o-chlorophenol, before analysis with the GC. The temperature programming sequence starts with an isothermal hold at 70°C for two minutes followed by programming to 170°C at 4°/min. Total GC analysis time is about 30 minutes. The injector and interface temperatures are maintained at 200°C. A Teflon column packed with 10% OS 138/H_3PO_4/SP-1200 on Chromosorb W AW is used for separating phenols. One microliter of the external standard and 1 $\mu\ell$ of each sample is injected into the GC. The data obtained from the GC computer system is used to calculate concentrations of phenols.

The linear range of each phenol found in exhaust and of the internal standard was determined. The concentrations of phenols fall well within the linear range. Should a sample be too concentrated it can be diluted volumetrically to a level within the linear range.

Several factors contribute to the overall recovery of phenols from exhaust. These include the stability of phenols traveling from automobile to impingers and the trapping and extraction efficiency of phenols. The results from the qualification tests indicate that approximately 100 percent of phenol injected into exhaust is recovered. One hundred percent phenol is also captured in two impingers connected in series. Extraction efficiency, however, is only about 68 percent. This low value is probably due to losses encountered in the drying process. Injection variability of phenol into the GC was only 2.2 percent for a series of five injections. Similar results are expected for the other phenols found in exhaust.

Several methods for the determination of phenols in automobile exhaust were combined and adapted to the needs of this project. The resulting procedure used to measure phenols is sensitive to about 1 $\mu g/m\ell$. The phenols in order of elution are phenol; salicylaldehyde; m-cresol and p-cresol; p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol and 2,4,6-trimethylphenol; 2,3,5-trimethylphenol and 2,3,5,6-tetramethylphenol. Overall this procedure should provide a relatively accurate method for determining the concentrations of the phenols in dilute exhaust, and its use is recommended for this project.

SECTION 12

THE QUALIFICATION EXPERIMENT

Qualification experiments were carried out to determine what fraction of the unregulated pollutants entering the dilution tunnel could be recovered at the sampling point. A constant flow of each unregulated pollutant was injected from a pressurized cylinder into the dilution tunnel-CVS system at the point raw exhaust normally enters the dilution tunnel (Figure 57). The CVS diluted samples were extracted from the dilution tunnel-CVS system with a multiport sampling probe at a point after the orifice plate on the tunnel and before the CVS system. All qualified unregulated pollutants were sampled at this point except for nitrous oxide which was taken as a bag sample at the CVS (Figure 57).

Experiments were carried out with and without diesel exhaust present in the dilution tunnel-CVS system. A Mercedes 240D driving over a hot FTP (23-minute test) driving cycle was used to generate diesel exhaust for the experiments. Baseline emission levels of each pollutant from the Mercedes 240D were measured in order to correct recovery values for pollutants present in the exhaust.

The gaseous unregulated pollutants were injected into the dilution tunnel by the system shown in Figures 58 and 59. The pollutant passed through a needle valve to regulate flow, a flowmeter to monitor flowrate, and a dry gas meter to measure the injected volume of pollutant, before entering the dilution tunnel. A thermocouple was used to monitor the temperature of the injected gas, and a magnehelic gauge was used to monitor the pressure of gas passing through the injection system. This pressure was positive and generally recorded 0-2" of water. The phenols were injected into the dilution as a water solution using the modified mist generator shown in Figure 60. The test sequence developed to determine pollutant recovery consisted of a 23-minute continuous sampling period (pollutant injected with or without exhaust present) followed by a 10-minute soak period with the CVS off (no pollutant injected). During this time, impingers, bags or traps were changed to collect the next sample. After the soak period the test sequence was repeated until three to four sampling periods were completed. During each sampling period, three replicate impinger samples (aldehydes, total cyanide, organic amines, sulfur dioxide, ammonia, hydrogen sulfide--two for phenols), or two trap samples (organic sulfides) or one bag sample (nitrous oxide) were taken.

Nominal injected pollutant flows into the tunnel were 0.35 cu ft/min while nominal CVS flows were 300 cu ft/min. This gave an approximate 850 to 1 dilution. Percent recoveries were determined by analyzing the recovered

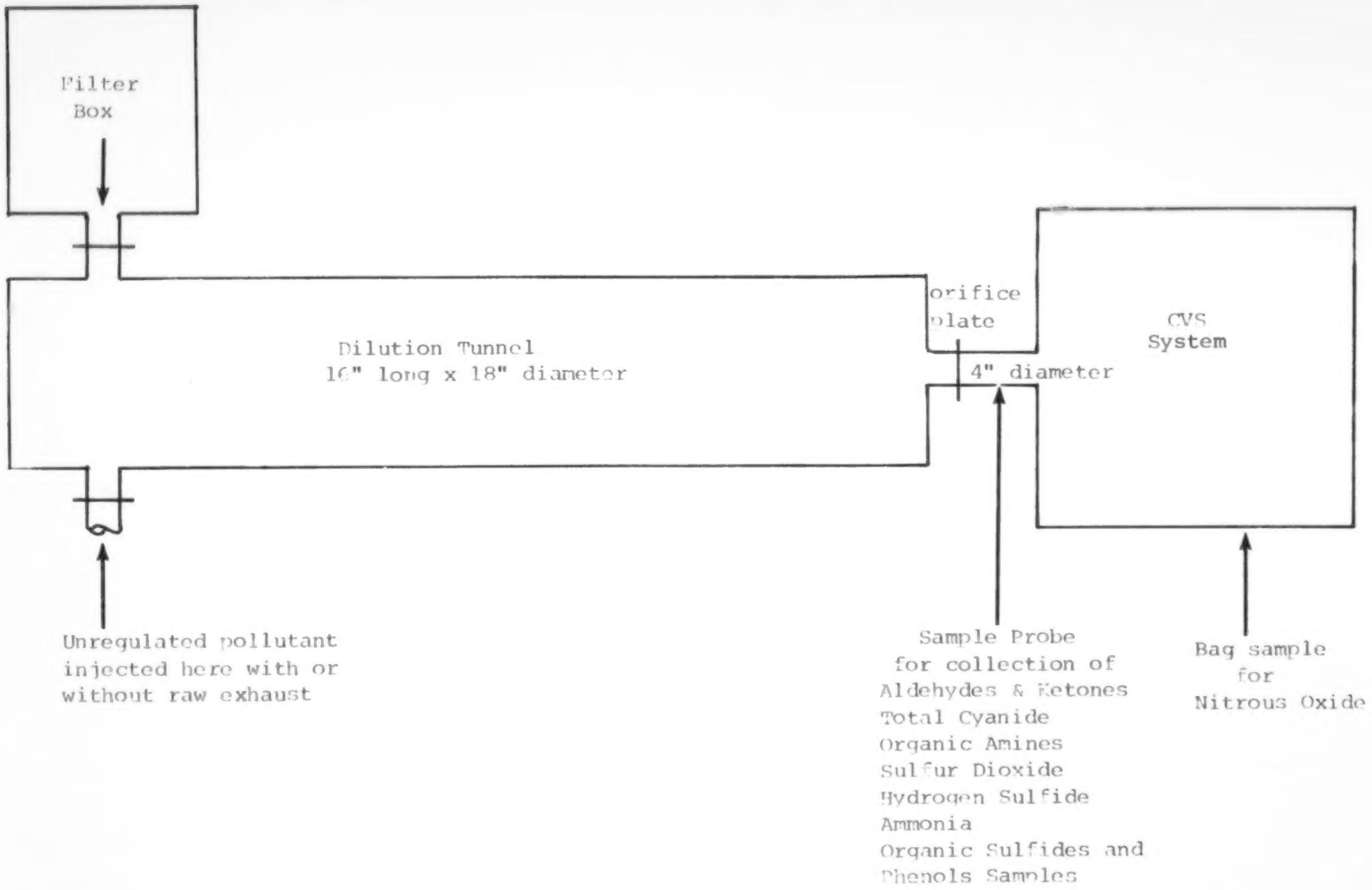

Filter
Box
Dilution Tunnel
16" long x 18" diameter
orifice
plate
4" diameter
CVS
System
Unregulated pollutant
injected here with or
without raw exhaust
Sample Probe
for collection of
Aldehydes & Ketones
Total Cyanide
Organic Amines
Sulfur Dioxide
Hydrogen Sulfide
Ammonia
Organic Sulfides and
Phenols Samples
Bag sample
for
Nitrous Oxide

Figure 57. Dilution tunnel-CVS system used in qualification experiments.

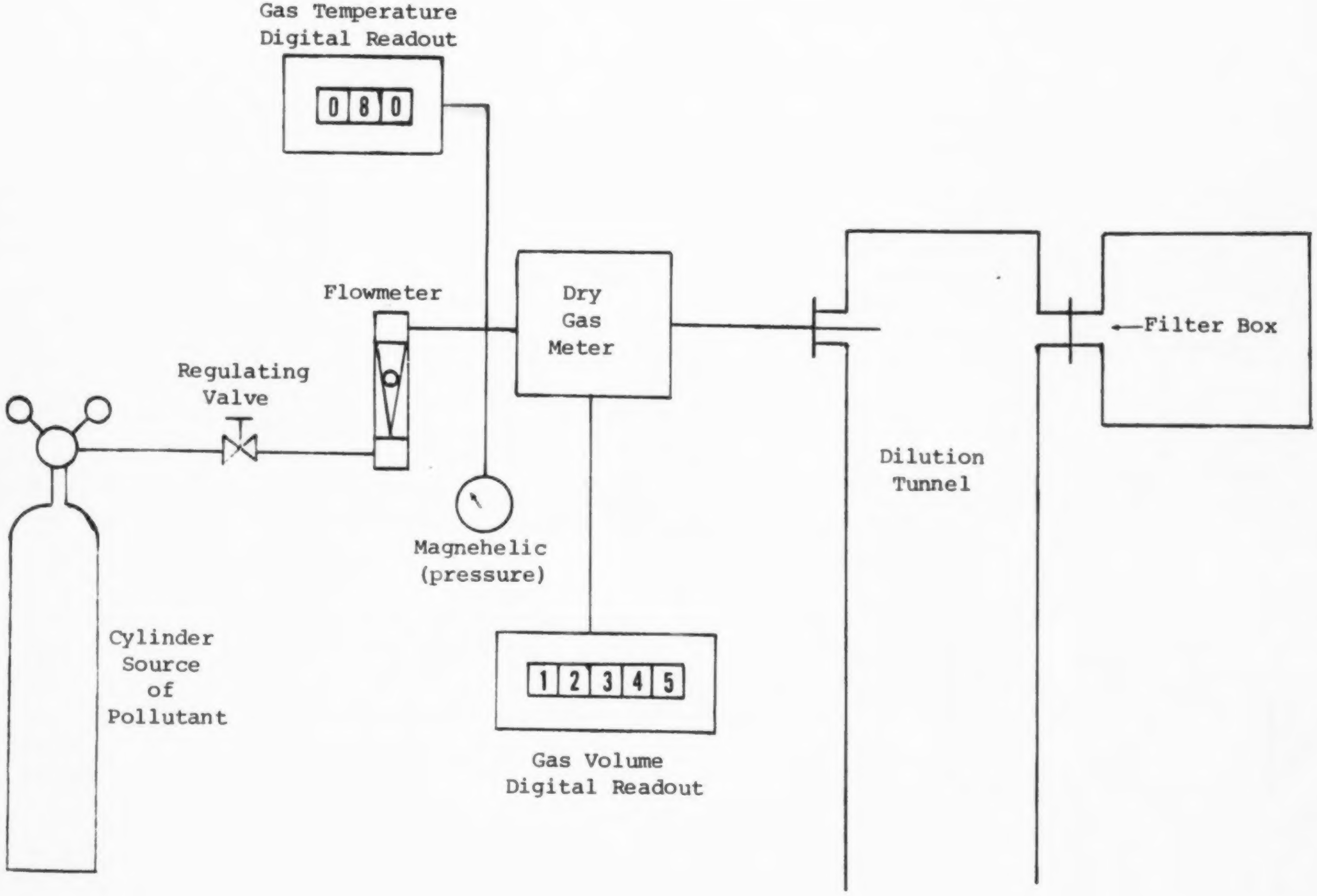

Gas Temperature
Digital Readout
080
Flowmeter
Regulating
Valve
Dry
Gas
Meter
Magnehelic
(pressure)
Cylinder
Source
of
Pollutant
12345
Gas Volume
Digital Readout
Dilution
Tunnel
Filter Box

Figure 58. Apparatus for injection of pollutant into dilution tunnel without exhaust.

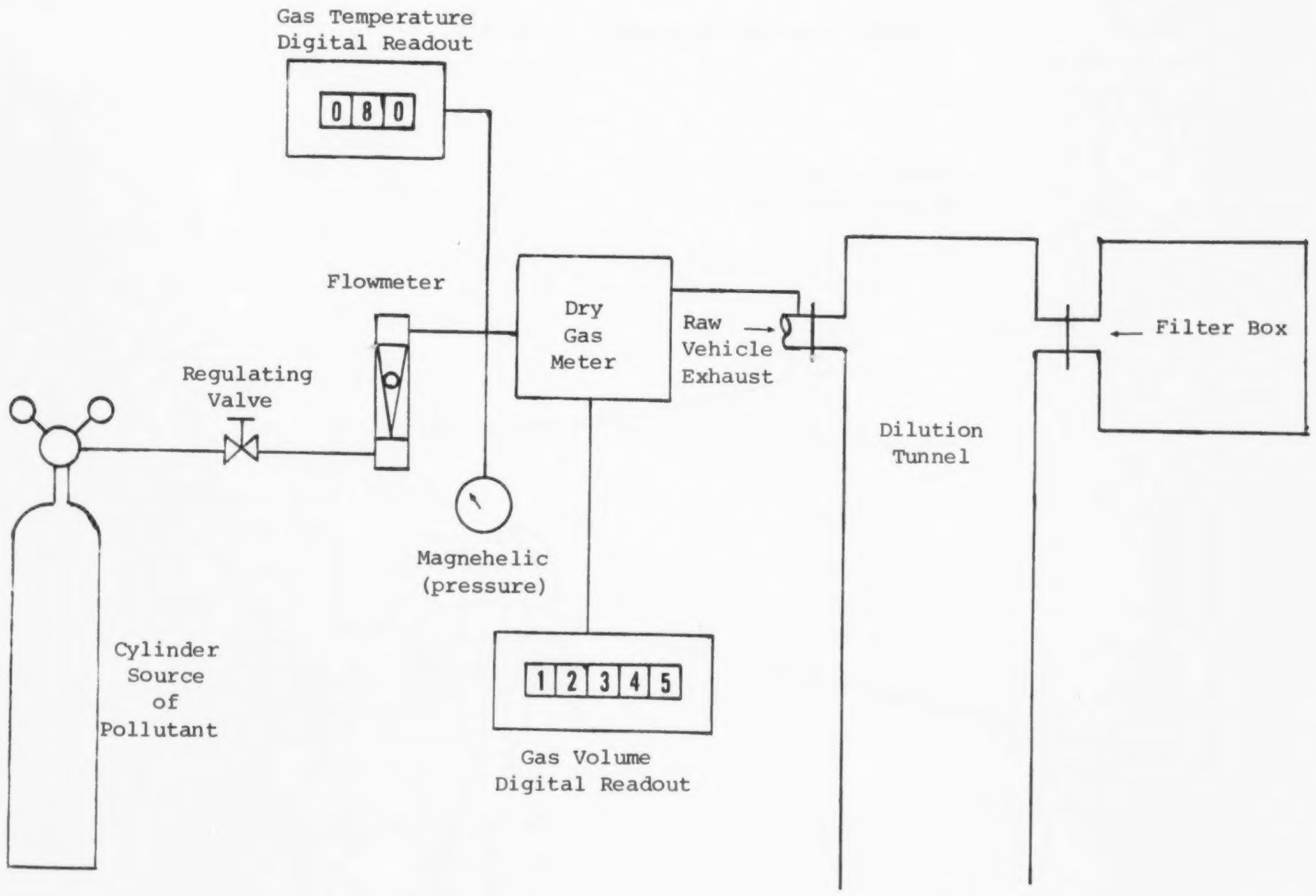

Gas Temperature
Digital Readout
080
Flowmeter
Regulating
Valve
Dry
Gas
Meter
Raw Vehicle Exhaust
Filter Box
Dilution
Tunnel
Magnehelic
(pressure)
Cylinder
Source
of
Pollutant
12345
Gas Volume
Digital Readout

Figure 59. Apparatus for injection of pollutant into dilution tunnel with exhaust.

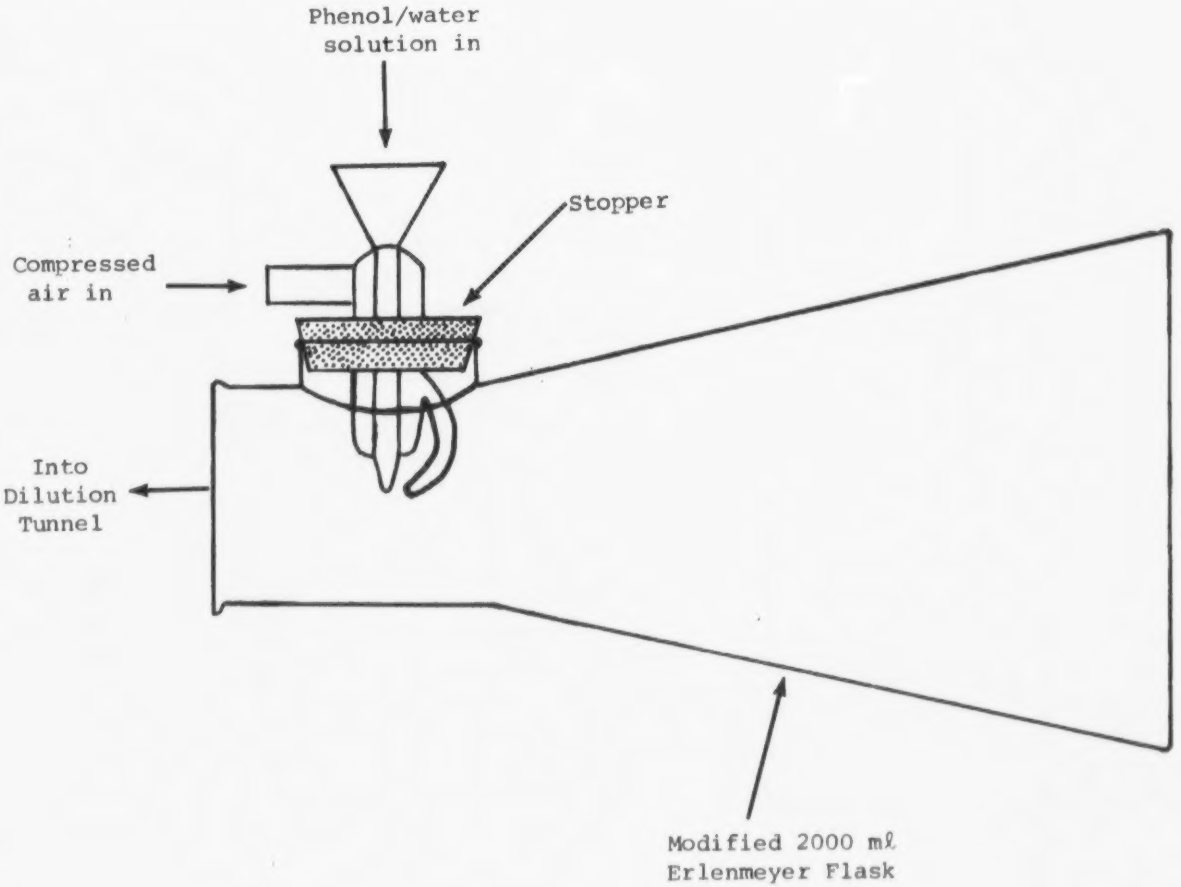

Phenol/water solution in
Stopper
Compressed air in
Into Dilution Tunnel
Modified 2000 mℓ Erlenmeyer Flask

Figure 60. Modified mist generator.

diluted sample, multiplying by the CVS dilution and dividing by the actual injected pollutant concentration.

SECTION 13

RESULTS AND CONCLUSIONS

To determine the suitability of the analytical procedures initially selected for dilute exhaust analysis, validation and qualification experiments were carried out. The validation experiments determined if the sampling and instrument parameters were appropriate for the quantitative analysis of dilute exhaust. The qualification experiments determined if the compounds of interest could be quantitatively recovered from the CVS tunnel with and without the presence of exhaust in the tunnel. The analytical procedures to be used in this project are listed in Table 65 along with methods of sampling and analysis. Table 65 also lists the validation and qualification experiments that were carried out.

The sampling parameters for all procedures were found to be adequate for the collection of each of the unregulated emissions. All samples, with the exception of the organic sulfides and hydrogen sulfide are stable for several days and can be stored and rerun within hours after sampling to prevent loss of sample integrity. All instruments demonstrate linearity of response for expected concentration ranges (sample concentrations above the linear range must be diluted to concentrations that fall within the linear range of the instrument). The organic sulfides must be monitored carefully as traps containing over 200 ng of sample fall beyond the linear range of the FPD. The sample flow rate can be lowered to prevent overloading the Tenax trap. Test-to-test repeatabilities for all procedures are documented in this report. In most cases, repeatability is difficult to obtain at the lower concentrations, while the repeatability at high concentrations is easily obtained. Interferences were checked and documented for each procedure. Phthalates were found to interfere with the aldehyde and ketone procedure and may cause erroneous results for crotonaldehyde. In the hydrogen sulfide procedure, sulfur dioxide decreases the apparent hydrogen sulfide concentration, and its presence or absence must be recorded. The other procedures have interferences that can be avoided if care is taken.

Qualification experiments were carried out on the aldehyde and ketone, organic amine, sulfur dioxide, nitrous oxide, hydrogen sulfide, total cyanide, organic sulfide, ammonia and phenol procedures to determine the recovery of known amounts of each pollutant from the CVS tunnel with and without exhaust (phenols CVS tunnel with exhaust only). Aldehydes and ketones, sulfur dioxide, nitrous oxide, total cyanide and phenols can be recovered quantitatively from the CVS tunnel with and without (not done for phenols) exhaust. There is a 10 percent loss of hydrogen sulfide with and without exhaust present. The organic amines, ammonia, and the organic sulfides experience significant losses in the CVS tunnel with and without exhaust. These losses must be taken into account when determining the concentration of these com-

TABLE 65. ANALYTICAL PROCEDURES FOR EMISSIONS CHARACTERIZATION

Compounds	Sampling	Analysis	Validation	Qualification
Aldehdyes and Ketones	Impingers	DNPH	Yes	Yes
Organic Amines	Impingers	GC-NPD	Yes	Yes
Sulfur Dioxide	Impingers	Ion Chrom.	Yes	Yes
Nitrous Oxide	Bags	GC-ECD	Yes	Yes
Individual Hydrocarbons	Bags	GC-FID	Yes	Not required
Hydrogen Sulfide	Impingers	Meth. Blue	Yes	Yes
Hydrogen Cyanide + Cyanogen	Impingers	GC-ECD	Yes	Yes
Carbonyl Sulfide + Organic Sulfides	Traps	GC-FPD	Yes	Yes
Ammonia	Impingers	Ion Chrom.	Yes	Yes
Sulfate	Filters	BCA	Not required	Not required
DMNA	Traps	GC-MS @ RTI	Not required	Not required
Phenols	Impingers	GC-FID	Yes	Yes
BaP	Filters	Fluorescence @ EPA	Not required	Not required

pounds in exhaust.

The procedures discussed in this report are effective in collecting and analyzing dilute exhaust samples and are recommended for use in this project.

REFERENCES

1. Dietzmann, H. E., Smith, L. R., Parness, M. A., and Fanick, E. R., "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles." Report to Environmental Protection Agency under Contract No. 68-02-2497, February, 1979.

2. Muir, G. D. (Ed.), Hazards in the Chemical Laboratory, The Chemical Society, London, 1977.

3. Stump, F., Oxygenated Compounds in Automobile Exhaust-GAS CHROMATOGRAPHIC PROCEDURE, MSERB-ESRL-EPA, Research Triangle Park, North Carolina.

4. Roberts, R. M., Giblert, J. C., et al; An Introduction to Modern Experimental Organic Chemistry; Holt, Rinehart and Winston, Inc. 1974, pg. 470-471.

5. Weast, R. C. (Ed.), Handbook of Chemistry and Physics, 54 Edition, Division of the Chemical Rubber Co., 1973.

6. Sekerka, I., and Lechner, J. F., Water Res., Vol. 10, pg. 479, 1976.

7. Valentour, J. C., Aggarwal, V., and Sunshine, I., Anal. Chem., Vol. 46, pg. 924, 1974.

8. Dimitriades, B., and Seizenger, D. E., Environ. Sci. Tech., Vol. 5, No. 3, pg. 223, 1971.

9. Papa, L. J., Dinsel, D. L., et al; J. Gas Chromatog., Vol. 6, pg. 270, 1968.

10. Klosterman, D. L., and Sigsby, J. E., Environ. Sci. Tech., Vol. 1, pg. 309, 1967.

11. (a) Black, F. M., High, L. E., and Sigsby, J. E., J. Chromatog. Sci., Vol. 14, pg. 257, May 1976. (b) Communication between Mobile Source Emissions Research Branch, ESRL-EPA, Research Triangle Park, and Southwest Research Institute.

12. Braker, W., and Mossman, A. L., Matheson Gas Data Book, 5th Edition, East Rutherford, N.Y., 1971.

13. Hoshika, Y., Anal. Chem., Vol. 48, pg. 1716, 1976.

14. Hoshika, Y., J. Chromatog., Vol. 115, pg. 596, 1975.

15. Sze, Y. L., and Borke, M. L., Anal. Chem., Vol. 35, pg. 240, 1963.

16. O'Donnell, J. F., and Mann, C. K., Anal. Chem., Vol. 36, pg. 2097, 1964.

17. McCurdy, W. H., Jr., and Reiser, R. W., Anal. Chem., Vol. 38, pg. 795, 1966.

18. Smith, J. R. L., and Waddington, D. J., Anal. Chem., Vol. 40, pg. 522, 1977.

19. "Amine Analysis," Bulletin 737A, Supelco Co., Belefonte, Pa., 1973.

20. "Penwalt 223 Amine Packing," Alltech Associates, Arlington Heights, Ill.

21. Moffat, A. C., and Horning, E. C., Anal. Lett., Vol. 3, pg. 205, 1970.

22. Clarke, D. D., Wilk, S., et al; J. Gas Chromatog., pg. 310, 1966.

23. Mosier, A. R., Andre, C. E., et al; Environ. Sci. Tech., Vol. 7, pg. 642, 1973.

24. Burks, R. E., Jr., Baker, E. B., et al; J. Agr. Food Chem., Vol. 7, pg. 778, 1959.

25. Dunn, S. R., Simenhoff, M. L., et al; Anal. Chem., Vol. 48, pg. 41, 1976.

26. Gruger, E. H., Jr., J. Agr. Food Chem., Vol. 20, pg. 781, 1972.

27. Andre, C. E., and Mosier, A. R., Anal. Chem., Vol. 45, pg. 1971, 1973.

28. Umbreit, G. R., Nygren, R. E., and Testa, A. J., J. Chromatog., Vol. 43, pg. 25, 1969.

29. Keay, N. J., and Hardy, R., J. Scie. Food Agr., Vol. 23, pg. 9, 1972.

30. Bowen, B. E., Anal. Chem., Vol. 48, pg. 1584, 1976.

31. West, P. W., and Gaeke, G. C., Anal. Chem., Vol. 28, pg. 1816, 1956.

32. Adams, D. F., Corn, M., et al; "Methods of Air Sampling and Analysis," (Tentative Method of Analysis for Sulfur Dioxide Content of the Atmosphere (colorimetric), No. 42401-01-69T), pg. 447, Amer. Publ. Health Assn., Washington, D. C., 1972.

33. "ASTM Standards - Water, Atmospheric Analysis," ASTM Designation D291470T, Part 23, Am. Soc. Test. Mat., Philadelphia, Pa., 1972.

34. US EPA, Fed. Register, Vol. 36, No. 158, 15492, 1971.

35. Robinson, E., and Robbins, R. C., "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants," Final Report, SRI Project 6755 Supplement, Stanford Research Inst., Palo Alto, Calif., 1968.

36. Stern, A. C. (Ed.), Air Pollution, 3rd Edition, Academic Press, Inc., N.Y., 1976, Vol. 3, pg. 214.

37. Zurlo, N., and Griffini, A. M., Med. Lav., Vol. 53, pg. 330, 1962.

38. Scaringelli, F. P., Elfers, L., et al; Anal. Chem., Vol. 42, pg. 1818, 1970.

39. Pate, J. B., Ammons, B. E., et al; Anal. Chem., Vol. 37, pg. 942, 1965.

40. Pate, J. B., Lodge, J. P., Jr., et al; Anal. Chem., Vol. 34, pg. 1660, 1962.

41. Scaringelli, F. P., Saltzman, B. E., et al; Anal. Chem., Vol. 39, pg. 1709, 1967.

42. Hartman-Leddon, Philadelphia, Pa.

43. Stern, A. C. (Ed.), Air Pollution, 3rd Edition, Academic Press, Inc., N. Y., 1976, Vol. 3, pg. 214.

44. Urone, P., Evans, J. B., and Noyes, C. H., Anal. Chem., Vol. 37, pg. 1104, 1965.

45. Bostrom, C. E., Int. J. Air Water Poll., Vol. 9, pg. 333, 1965.

46. Attari, A., Igielski, T. P., et al; Anal. Chem., Vol. 42, pg. 1282, 1970.

47. Kawai, T., Netsu Kanri, Vol. 22, pg. 20, 1970.

48. Thomas, M. D., Ivie, J. O., et al; Ind. Eng. Chem., Anal. Ed., Vol. 18, pg. 383, 1946.

49. Yocum, J. E., Richardson, R. L., et al; Proc. 49th Ann. Meet. Air Poll. Contr. Assn., Pittsburgh, Pa., 1956.

50. Kuczynski, E. R., Environ. Sci. Tech., Vol. 1, pg. 68, 1967.

51. Shikiya, J. M., and McPhee, R. D., 61st Annual Meeting, Paper No. 68-72, Air Poll. Contr. Assn., Pittsburgh, Pa., 1968.

52. Jacobs, M. B., The Chemical Analysis of Air Pollutants, Chapter 8, Wiley (Interscience), New York, N.Y., 1960.

53. Jacobs, M. B., The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents, Chapter 9, Wiley (Interscience), New York, N.Y., 1949.

54. Katz, M., Anal. Chem., Vol. 22, pg. 1040, 1950.

55. Stratman, H., Mikrochim. Acta., Vol. 6, pg. 688, 1954.

56. Pate, J. B., Lodge, J. P., Jr., et al; Anal. Chim. Acta., Vol. 28, pg. 341, 1963.

57. Lodge, J. P., Jr., Pate, J. B., et al; Amer. Ind. Hyg. Assn. J., Vol. 24, pg. 380, 1963.

58. Forrest, J., and Newman, L., Atmos. Environ., Vol. 7, pg. 561, 1973.

59. Huygen, C., Anal. Chim. Acta., Vol. 28, pg. 349, 1963.

60. Harding, J., and Schlein, B., "Nuclear Techniques in Environmental Pollution," SM-142a/0, IAEA, Vienna, Austria, 1971.

61. Wilson, B. H., and McConnell, F. J., J. Soc. Chem. Ind., Vol. 53, pg. 385, 1934.

62. Huey, N. A., J. Air Poll. Cont. Assn., Vol. 18, pg. 610, 1968.

63. Thomas, F. W., and Davidson, C. M., J. Air Poll. Cont. Assn., Vol. 11, pg. 1, 1961.

64. Stalker, W. W., Dickerson, R. C., et al; Amer. Ind. Hyg. Assn. J., Vol. 24, pg. 68, 1963.

65. Hickey, H. R., and Hendrickson, E. R., J. Air Poll. Cont. Assn., Vol. 15, pg. 409, 1965.

66. Harding, C. I., and Kelley, T. R., J. Air Poll. Cont. Assn., Vol. 17, pg. 545, 1967.

67. Ikeda, T., J. Hyg. Chem., Vol. 13, pg. 41, 1967.

68. Stevens, R. K., Mulik, J. D., et al; Anal. Chem., Vol. 43, pg. 827, 1971.

69. Stevens, R. K., O'Keeffe, A. E., et al; Environ. Sci. Tech., Vol. 3, pg. 652, 1969.

70. Ronkainen, P., Denslow, J., et al; J. Chromatog. Sci., Vol. 11, pg. 384, 1973.

71. Pecsar, R. E., and Hartmann, C. H., J. Chromatog. Sci., Vol. 11, pg. 492, 1973.

72. Stevens, R. K., and O'Keeffe, A. E., Anal. Chem., Vol. 42, pg. 143a, 1970.

73. Bruner, F., Liberti, A., et al; Anal. Chem., Vol. 44, pg. 2070, 1972.

74. Bruner, F., Ciccioli, P., et al; Anal. Chem., Vol. 47, pg. 141, 1975.

75. DeSouza, T. L. C., Lane, D. C., et al; Anal. Chem., Vol. 47, pg. 543, 1975.

76. Bruner, F., Ciccioli, P., et al; J. Chromatog., Vol. 99, pg. 661, 1974.

77. Bremner, J. M., and Banwart, W. L., Sulfur Inst. Journal, Vol. 10, pg. 6, 1974.

78. Mulik, J. D., Todd, G., et al; "Ion Chromatography Determination of Atmospheric Sulfur Dioxide," Symposium on Ion Chromatograph Analysis of Environmental Pollutants, EPA, Research Triangle Park, North Carolina, April, 1977.

79. Dietzmann, H. E., "Protocol to Characterize Gaseous Emissions as a Function of Fuel and Additive Composition," Environmental Protection Technology Series under Contract 68-02-1275, September, 1975.

80. Stern, A. C. (Ed.), Air Pollution, Third Edition, Volume III, Academic Press, New York, 1976, pg. 275.

81. Private communication between R. B. Zweidinger and Frank Black of EPA, Research Triangle Park, and Harry Dietzmann of Southwest Research Institute.

82. Bethea, R. M., J. Air Poll. Cont. Assoc., Vol. 23, pg. 710, 1973.

83. Bamesberger, W. L., and Adams, D. F., Tappi, Vol. 52, pg 1302, 1969.

84. "Hydrogen Sulfide in Air Analytical Method," H.L.S., Vol. 12, pg. 362, 1975.

85. Bamesberger, W. L., and Adams, D. F., Environ. Sci. Tech., Vol. 3, pg. 258, 1969.

86. Gustafsson, L., Talanta, Vol. 4, pg. 227, 1960.

87. Moest, R. R., Anal. Chem., Vol. 47, pg. 1204, 1975.

88. Buck, M., and Gies, H., Staub, Vol. 26, pg. 27, 1966.

89. Jacobs, M. B., Braverman, M. M., and Hochheiser, S., Anal. Chem., Vol. 29, pg. 1349, 1957.

90. Cave, G. C. B., Tappi, Vol. 46, pg. 1, 1963.

91. Budd, M. S., and Bewick, H. A., Anal. Chem., Vol. 24, pg. 1536, 1952.

92. Bostrom, C., Air and Water Poll. Int. J., Vol. 10, pg. 435, 1966.

93. Flamm, D. L., and James, R. E., Environ. Sci. Tech., pg. 159, 1975.

94. Adams, D. F., Bamesberger, W. L., et al; J. Air Poll. Cont. Assn., Vol. 18, pg. 145, 1968.

95. Stecher, P. G. (Ed.), The Merck Index, 8th Edition, Merck and Company, Inc., Rahway, N. J., 1968, pg. 64.

96. Masterton, W. L., and Slowinski, E. J., Chemical Principles, 3rd Edition, W. B. Saunders Company, Philadelphia, Pa., 1973.

97. Carter, R. V., et al; Air Pollution Engineering Source Evaluation of Ammonia Oxidation Plant Number 10, Holston Army Ammunition Plant, Kingsport, Tennessee, Army Construction Engineering Research Lab., Champaign, Ill., 1974, pg. 10.

98. Healy, T. V., and Pilbeam, A., Ammonia and Related Atmospheric Pollutants at Harwell Part 1. Techniques for hourly sampling and analysis of pollutants, Applied Chemistry Division, Atomic Energy Research Establishment, Harwell, Berkshire, 1972.

99. Kothny, E. L., Intersociety Committee, Health Lab. Sci., Vol. 10, pg. 115, 1973.

100. Okita, T., and Kanomori, S., Atmos. Environ., Vol. 5, pg. 622, 1971.

101. Kramer, D. N., and Sech, J. M., Anal. Chem., Vol. 44, pg. 395, 1972.

102. Zitomer, F., and Laumbert, J. L., Anal. Chem., Vol. 34, pg. 1738, 1962.

103. Blinn, R. C., and Gunther, F. A., Anal. Chem., Vol. 29, pg. 1882, 1957.

104. Williams, D. D., and Miller, R. R., Anal. Chem., Vol. 34, pg. 225, 1962.

105. Gunther, F. A., Barkley, J. H., et al; Anal. Chem., Vol. 28, pg 1985, 1956.

106. Kolbezen, M. J., Eckert, J. W., et al; Anal. Chem., Vol. 36, pg. 593, 1964.

107. Pierson, R. H., Fletcher, A. A., et al; Anal. Chem., Vol. 28, pg. 1218, 1956.

108. Burns, E. A., The Analysis of Exhaust Gases Trapped from Ablating Nozzles, TRW Report No. 9840-6001-TU 000, Redordo Beach, Calif., 1964.

109. Howell, J. H., and Boltz, D. F., Anal. Chem., Vol. 36, pg. 1799, 1964.

110. Burns, E. A., Unpublished results, 1963.

111. Jenkins, R. W., Jr., Cheek, C. H., et al; Anal. Chem., Vol. 38, pg. 38, pg. 1257, 1966.

112. Miettinen, J. K., and Virtanen, A. I., Ann. Acad. Aci. Fennicae, Ser. A, II, No. 41, 1951, through Chem. Abst., Vol. 46, pg. 11500, 1952.

113. Arcand, G. M., and Swift, E. H., Anal. Chem., Vol. 28, pg. 440, 1956.

114. Krivis, A. F., Supp, G. R., et al; Anal. Chem., Vol. 35, pg. 2216, 1963.

115. Gilbert, T. R., and Clay, A. M., Anal. Chem., Vol. 45, pg. 1758, 1973.

116. Mertens, J., Van den Winkle, P., et al; Bull. Soc. Chem. Belg., Vol. 83/n° 1-2/, pg. 26, 1973.

117. Furman, N. H. (Ed.), Scott's Standard Methods of Chemical Analysis, 5th Edition, Van Nostrand, N. Y., 1958, Vol. 1, pg. 2336.

118. Vogel, A. I., Quantitative Inorganic Analysis, 3rd Edition, Longmans, Green, London, 1961, pg. 1092.

119. Steyermark, A., Quantitative Organic Microanalysis, Blakestone, N. Y., 1951, pg. 56.

120. Sadek, F. S., and Reilly, C. N., Anal. Chem., Vol. 31, pg. 494, 1959.

121. Crane, F. E., and Smith, E. A., Chemist-Analyst, Vol. 49, pg. 38, 1960.

122. Crane, F. E., and Smith, E. A., Chemist-Analyst, Vol. 52, pg. 105, 1963.

123. Hodges, J. A., Bell, J. P., et al; Joint Conf. on Sensing Environmental Pollutants Collected, Technical Papers, 1972, Vol. 1, 71-1067.

124. Sigsby, J. E., Jr., Black, F. M., et al; Environ. Sci. Tech., Vol. 7, pg. 51, 1973.

125. Spencer, C. F., Baumann, F., et al; Anal. Chem., Vol. 30, No. 9, pg. 1473, 1958.

126. Sumner, S., Karrman, K. J., et al; Mikrochim Acta, pg. 1144, 1956.

127. Liberti, A., and Cartoni, G. P., Chim. e ind., Vol. 39, pg. 821, 1957.

128. Ryce, S. A., and Bryce, W. A., Anal. Chem., Vol. 29, pg. 925, 1957.

129. Desty, D. H., and Whyman, B. H. F., Anal. Chem., Vol. 29, pg. 230, 1957.

130. Coleman, H. J., Thompson, C. C., et al; Anal. Chem., Vol. 30, pg. 1592, 1958.

131. Desty, D. H., and Harbourn, C. L. A., Div. of Analytical and Petroleum Chemistry, Symposium on Advances in Gas Chromatography, 132nd meeting, ACS, New York, N. Y., September, 1957.

132. Amberg, C. H., Can. J. Chem., Vol. 36, pg. 590, 1958.

133. Sullivan, J. H., Walsh, J. T., et al; Anal. Chem., Vol. 31, pg. 1827, 1959.

134. Dal Nogare, S., and Bennett, C. E., Anal. Chem., Vol. 30, pg. 1157, 1958.

135. Harrison, G. F., Knight, P., et al; Second Int'l Symposium on Gas Chromatograph, Amsterdam, May, 1958.

136. Adams, D. F., and Koppe, R. K., Tappi, Vol. 42, pg. 601, 1959.

137. Schols, J. A., Anal. Chem., Vol. 33, pg. 359, 1961.

138. Hall, H. L., Anal. Chem., Vol. 34, pg. 61, 1962.

139. Adams, D. F., Kippe, R. K., et al; Tappi, Vol. 43, pg. 602, 1960.

140. Feldstein, M., Balestrieri, S., et al; J. Air Poll. Cont. Assn., Vol. 15, pg. 215, 1965.

141. Fredericks, E. M., and Harlow, G. A., Anal. Chem., Vol. 36, pg. 263, 1964.

142. Kummer, W. A., Pitts, J. N., Jr., et al; Environ. Sci, Tech., Vol. 5, pg. 1045, 1971.

143. Mizany, A. I., J. Chromatog. Sci., Vol. 8, pg. 151, 1970.

144. Rasmussen, R. A., AM. Lab, Vol. 4, pg. 55, 1972.

145. Brody, S. S., and Chaney, J. E., J. Gas Chromatog., Vol. 4, pg. 42, 1966.

146. Bruner, F., Liberti, A., et al; Anal. Chem., Vol. 44, pg. 2070, 1972.

147. Elliott, L. F., and Travis, T. A., Soil Sci. Soc. Amer. Proc., Vol. 37, pg. 700, 1973.

148. Francis, A. J., Adamson, J., et al; Bull. Ecol. Res. Comm., (Stockholm), Vol. 17, pg. 485, 1973.

149. Lewis, J. A., and Papavizas, G. C., Soil Biol. Biochem., Vol. 2, pg. 239, 1970.

150. Lovelock, J. E., Maggs, R. J., et al; Nature, London, Vol. 237, pg. 452, 1972.

151. Ronkainen, P., Denslow, J., et al; J. Chromatog. Sci., Vol. 11, pg. 384, 1973.

152. Stanley, T. W., Sawicki, E., Johnson, H., and Pfaff, J. D., Mikrochim, Acta, Vol. 1, pg. 48, 1965.

153. Umbreit, G., and Houtman, R. L., Journal of Pharmaceutical Sciences, Vol. 56, pg. 349, 1967.

154. Afghan, B. K., Belliveau, P. E., Larose, R. H., and Ryan, J. F., Analytica Chimica Acta, Vol. 71, pg. 355, 1974.

155. Lawrence, J. F., Journal of Chromatographic Science, Vol. 17, pg. 147, 1979.

156. Wolkoff, A. W., and Larose, R. H., Journal of Chromatography, Vol. 99, pg. 731, 1974.

157. Sheffer, H. E., Perry, R. L., Thimineur, R. J., Adams, B. T., Simonian, J. L., Zutty, N. L., and Clendenning, R. A., Ind. Eng. Chem. Prod. Res. Develop., Vol. 10, pg. 362, 1971.

158. Shulgin, A., Analytical Chemistry, Vol. 36, pg. 920, 1964.

159. Argauer, R. J., Analytical Chemistry, Vol. 40, pg. 122, 1968.

160. Heenan, M. P., and McCallum, N. K., Journal of Chromatographic Science, Vol. 12, pg. 89, 1974.

161. Kawahara, F. K., Analytical Chemistry, Vol. 40, pg. 1009, 1968.

162. Cohen, I. C., Norcup, J., Ruzicka, H. A., and Wheals, B. B., J. Chromatog., Vol. 44, pg. 251, 1969.

163. Seiber, J. N., Crosby, D. G., Fouda, H., and Soderquist, C. J., J. Chromatog., Vol. 73, pg. 89, 1972.

164. Bartle, K. D., Elstub, J., Novotny, M., and Robinson, R. J., Journal of Chromatography, Vol. 135, pg. 351, 1977.

165. Ma, T. S., and Speigel, D., Microchemical Journal, Vol. 10, pg. 61, 1966.

166. Mindrup, R., Jr., Industrial Research/Development, pg. 79, August, 1978.

167. Chriswell, C. D., Chang, R. C., and Fritz, J. S., Analytical Chemistry, Vol. 47, pg. 1325, 1975.

168. Braithwaite, B., and Penketh, G., Analytical Chemistry, Vol. 36, pg. 185, 1964.

169. Landault, C., and Guiochen, G., Analytical Chemistry, Vol. 39, pg. 713, 1967.

170. Fisher, G. E., and Neerman, J. C., I and EC Product Research and Development, Vol. 5, pg. 288, 1966.

171. Bark, L. S., and Clarke, K. F., J. Chromatog., Vol. 48, pg. 418, 1970.

172. Di Corcia, A., Journal of Chromatography, Vol. 80, pg. 69, 1973.

173. Preston, S. T., A Guide to the Analysis of Phenols by Gas Chromatography, PolyScience Corporation, Niles, Illinois, 1966.

174. Eichelberger, J. W., Dressman, R. C., and Longbottom, J. E., Environmental Science and Technology, Vol. 4, pg. 576, 1970.

175. Yrjanheikki, Erkki, Am. Ind. Hyg. Assoc. J., Vol. 39, pg. 326, 1978.

176. Brown, R. A., Searl, T. D., King, W. H., Jr., Dietz, W. A., and Kelliher, J. M., Rapid Methods of Analysis for Trace Quantities of Polynuclear Aromatic Hydrocarbons and Phenols in Automobile Exhaust, Gasoline and Crankcase Oil, Final Report for CRC - APRAC Project CAPE-12-68, Esso Research and Engineering Company, Linden, N.J., 1973.

177. Barber, E. D., Sawicki, E., and McPherson, S. P., Analytical Chemistry, Vol. 36, pg. 2442, 1964.

178. Crouse, R. H., Garner, J. W., and O'Neill, H. J., J. of G.C., pg. 18, February, 1963.

179. Spears, A. W., Analytical Chemistry, Vol. 35, pg. 320, 1963.

APPENDIX A

ALDEHDYE AND KETONE PROCEDURE

THE MEASUREMENT OF ALDEHYDES AND KETONES IN EXHAUST

The aldehydes and ketones that are included in this analysis are: formaldehyde, acetaldehyde, acetone (acetone, acrolein, and propionaldehyde are not resolved from each other under normal operating conditions and all three are reproted together as acetone), isobutyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde. The measurement of the aldehydes and ketones in exhaust is accomplished by bubbling the exhaust through glass impingers containing 2,4 dinitrophenylhydrazine (DNPH) in dilute hydrochloric acid. The exhaust sample is collected continuously during a test cycle. The aldehydes and ketones (also known as carbonyl compounds) react with the DNPH to form their respective phenylhydrazone derivatives. These derivatives are insoluble or only slightly soluble in the DNPH/HCl solution and are removed by filtration followed by pentane extractions. The filtered percipitate and the pentane extracts are combined and the pentane is removed by evaporation in the vacuum oven. The remaining dried extract contains the phenylhydrazone derivatives. The extract is dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. A portion of this dissolved extract is injected into a gas chromatograph and analyzed using a flame ionization detector. The detection limits for this procedure under normal operating conditions are on the order of 0.005 ppm carbonyl compound in dilute exhaust.

SAMPLING SYSTEM

Two glass impingers in series, each containing 40 mℓ of 2 N HCl-2,4 dinitrophenylhydrazine, are used to collect exhaust samples for the analysis of the aldehydes and ketones. A flow schematic of the sample collection system is shown in Figure 1. The two impingers together trap approximately 98 percent of the carbonyl compounds. The temperature of the impinger is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4 ℓ/minute by the sample pump. A dry gas meter is used to determine the total flow through the impinger during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allows monitoring of the sample flow to insure proper flow rates during sampling. When sampling diesel fueled vehicles, a heated filter, located between the on-off solenoid valve and the dilution tunnel, is used to prevent diesel particulate from contaminating the sampling system. The filter and line connecting the filter to the dilution tunnel are heated to 375°F in order to prevent the aldehydes and ketones from being retained in the filter and sample line. The Teflon line connecting the

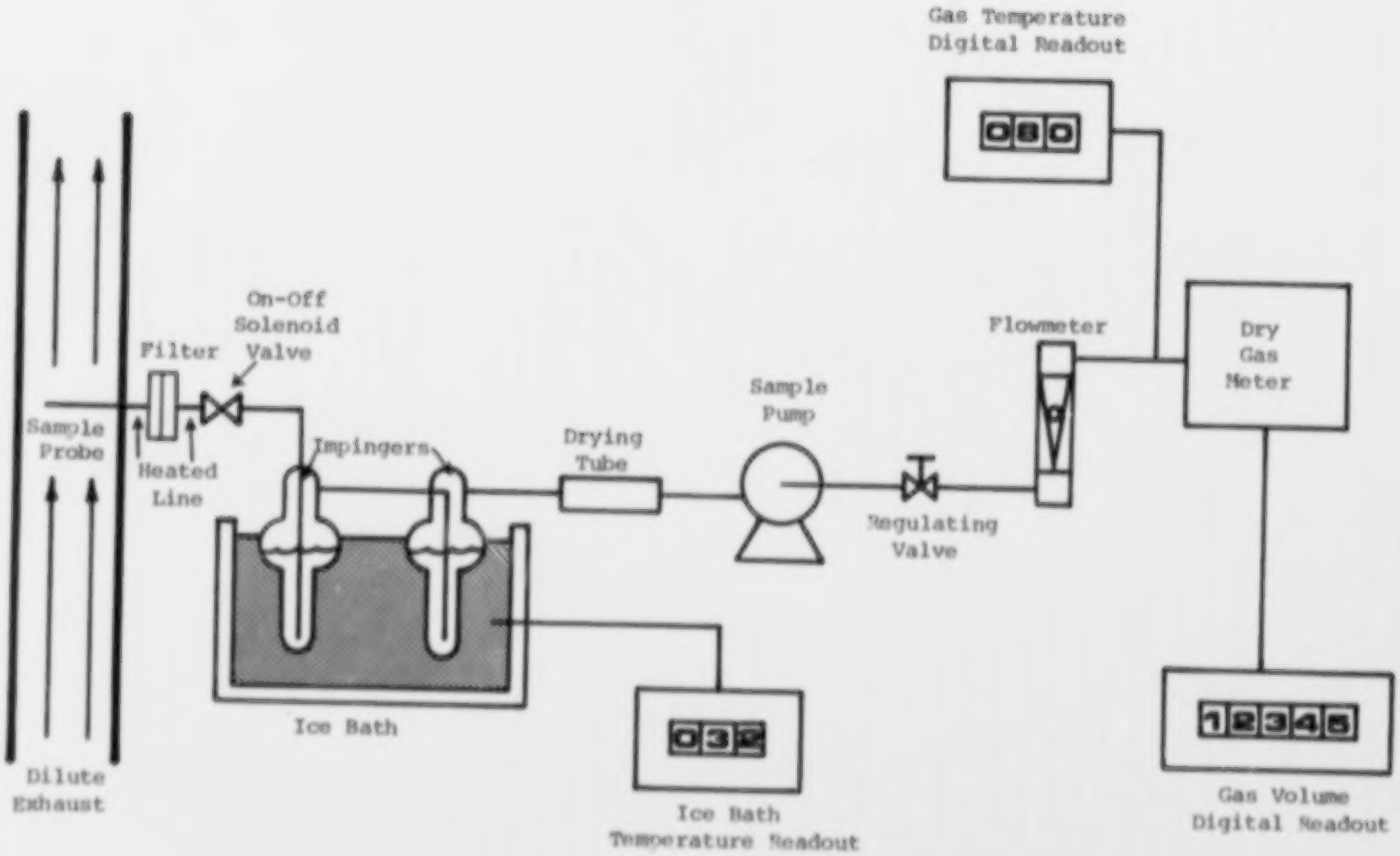

Gas Temperature
Digital Readout
080
On-Off
Solenoid
Valve
Filter
Flowmeter
Dry
Gas
Meter
Sample
Pump
Drying
Tube
Impingers
Sample
Probe
Heated
Line
Regulating
Valve
Ice Bath
032
Dilute
Exhaust
Ice Bath
Temperature Readout
12345
Gas Volume
Digital Readout

Figure 1. Aldehyde and ketone sample collection flow schematic.

heated filter and the solenoid valve is heated to ~175°F in order to prevent water from condensing in the sample line. Several views of the sampling system are shown in Figure 2.

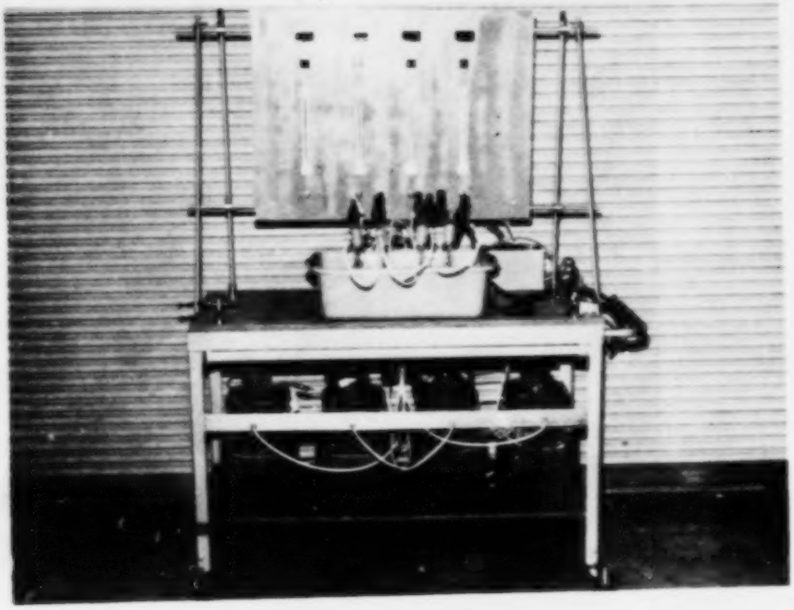
ANALYTICAL PROCEDURE

The analysis of the aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and of the ketones (acetone and methylethylketone) in dilute exhaust is accomplished by collecting these carbonyl compounds in a hydrochloric acid (HCl)/2,4 dinitrophenylhydrazine (DNPH) solution as their 2,4 dinitrophenylhydrazone derivatives. The derivatives are removed from the HCl/DNPH absorbing solution by filtration and/or extractions with pentane. The filtered precipitate and the pentane extracts are combined and the volatile solvents are removed. The remaining extract contains the phenylhydrazone derivatives. The derivatives are then dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. This solution is analyzed by injecting a small volume of the solution in to a gas chromatograph equipped with dual flame ionization detectors. From this analysis and the measured volume of exhaust sampled, the concentration of the carbonyl compounds in exhaust can be determined. The analysis flow schematic for the aldehydes and ketones is shown in Figure 3. A detailed description of the procedure follows.

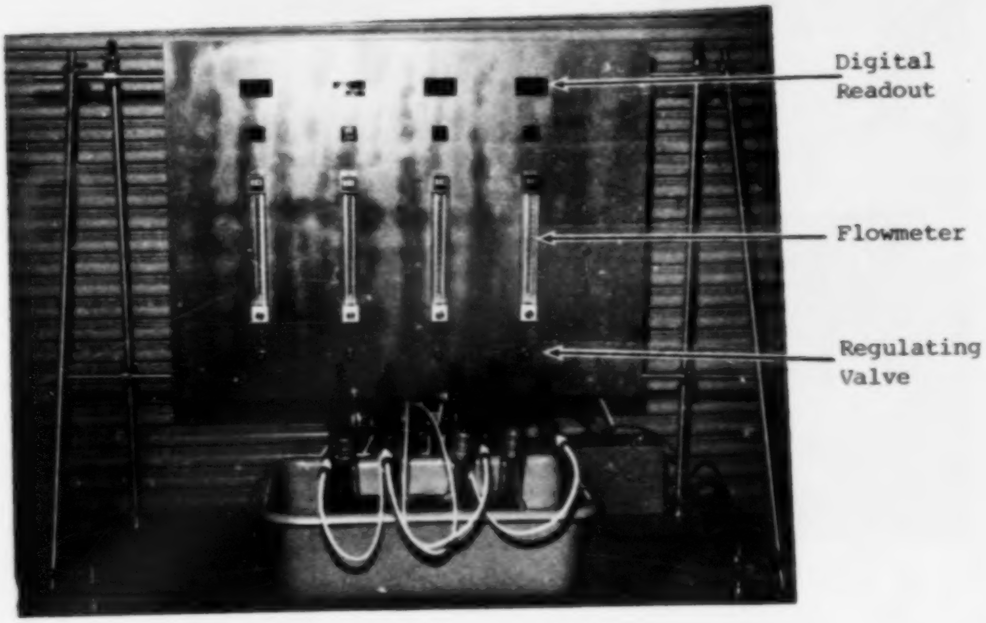
The aldehdyes and ketones are trapped in solution by bubbling a known volume of dilute exhaust through two glass impingers connected in series, with each impinger containing 40 mℓ of a 2 N HCl solution saturated with DNPH. The sampling temperature and barometric pressure are recorded during this bubbling period. The carbonyl compounds in the exhaust react with the DNPH to form slightly soluble or insoluble 2,4 dinitrophenylhydrazone derivatives. The two impingers together collect 98+ percent of the carbonyls that are present in the exhaust. The impingers are removed from the sampling cart and are allowed to stand at room temperature for at least one hour before proceeding to the filtration and extraction steps. Figure 4 shows two impingers containing the HCl/DNPH absorbing solution after being removed from the sampling cart.

Under normal operating conditions the contents of the two impingers are combined and analyzed as one sample. If either of the two impingers contain a precipitate they are first subjected to a filtration step. If no percipitate is present, this filtration step is omitted and the extraction step, described later in the procedure, is the first step.

For the filtration step, the contents of the two impingers are poured through a fritted glass filter into a flask under vacuum (Figure 5). The two impingers are rinsed with small portions of deionized water. This wash water is also poured through the fritted glass filter. The precipitate in the filter is then washed with a few mℓ of deionized water. The fritted filter is then removed from the flask containing the 80 mℓ of absorbing reagent and the water washings. The flask is then set aside for the ex-



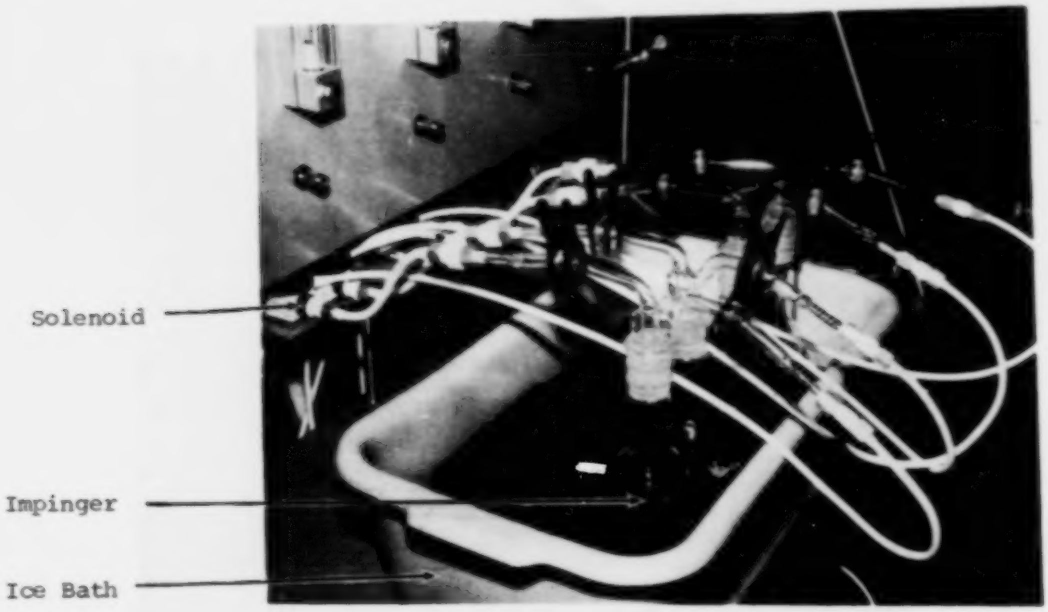
Front View



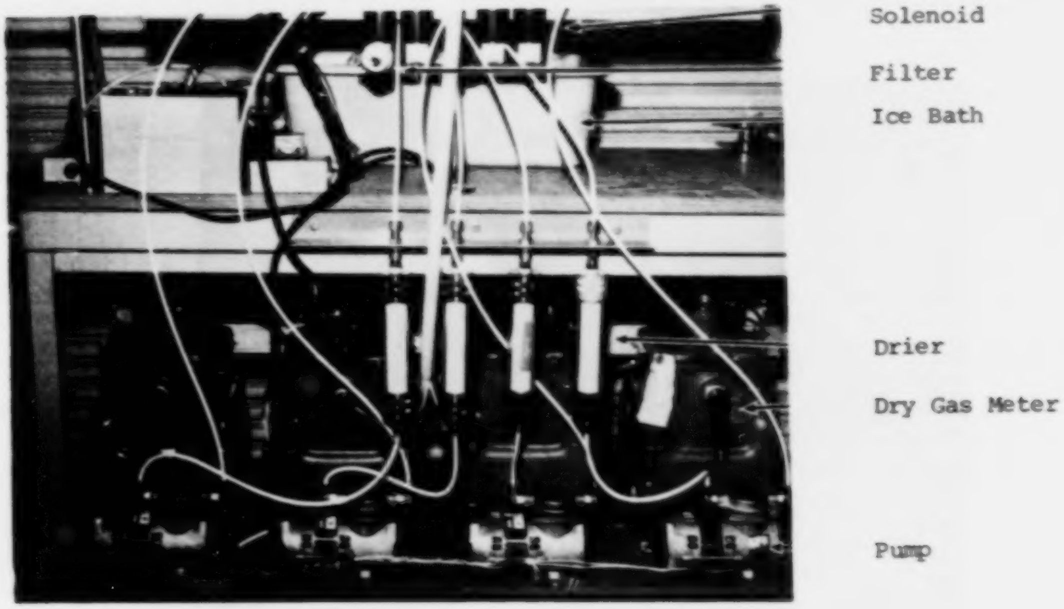
Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. Aldehyde and ketone sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). Aldehyde and ketone sampling system.

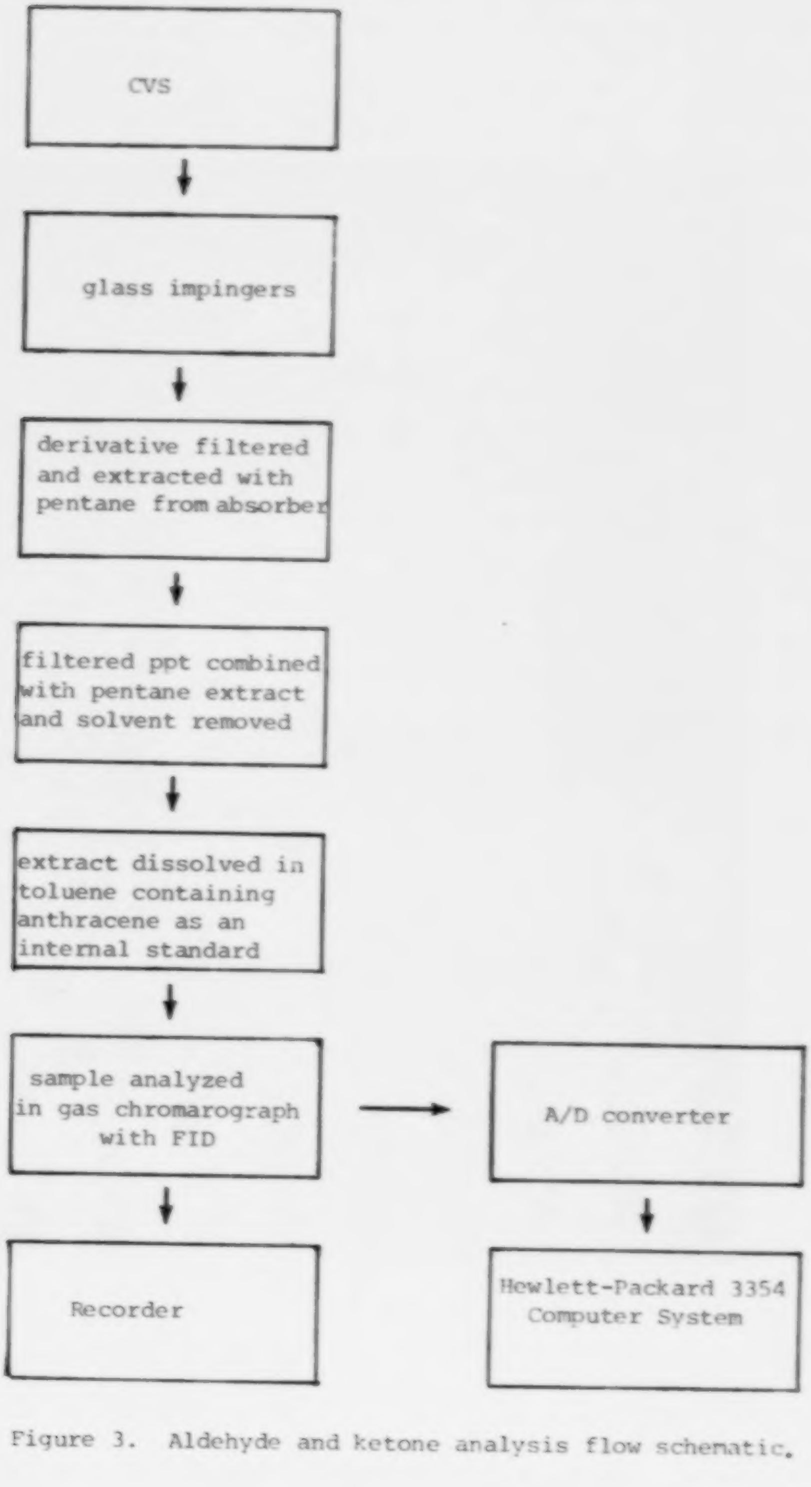

CVS
glass impingers
derivative filtered and extracted with pentane from absorber
filtered ppt combined with pentane extract and solvent removed
extract dissolved in toluene containing anthracene as an internal standard
sample analyzed in gas chromarograph with FID
A/D converter
Recorder
Hewlett-Packard 3354 Computer System

Figure 3. Aldehyde and ketone analysis flow schematic.

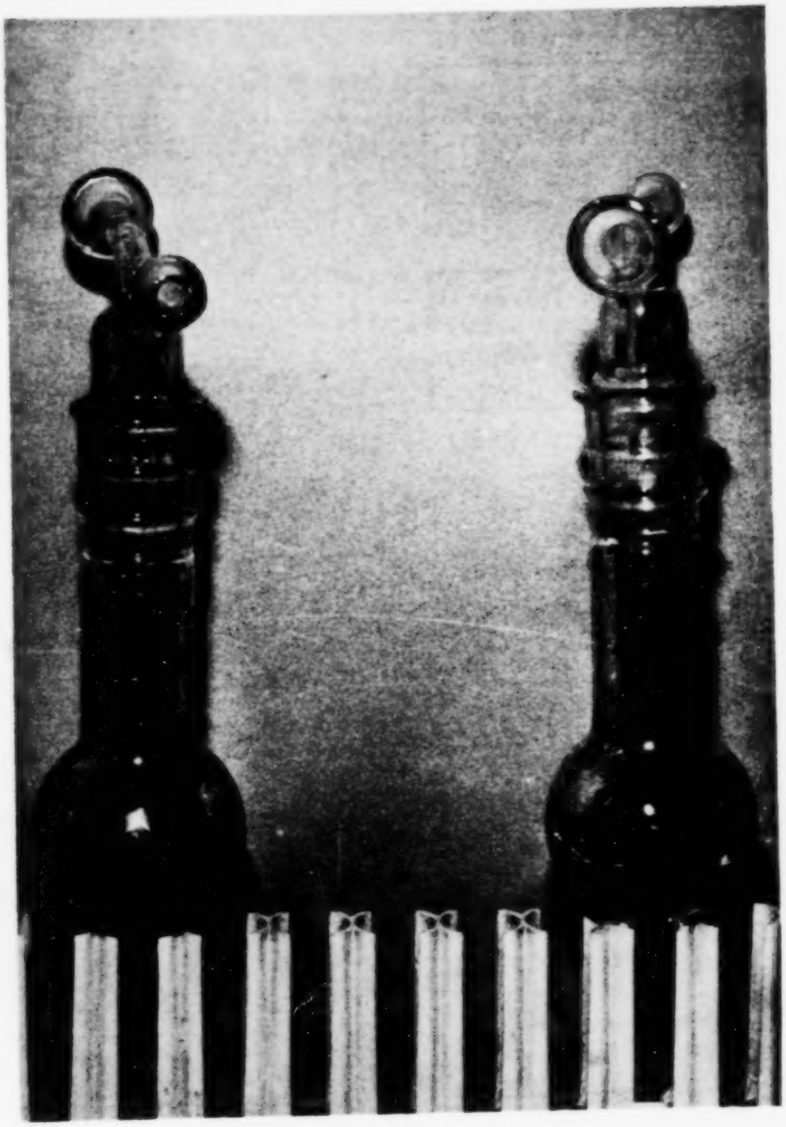


Figure 4. Impingers containing HCl/DNPH abosrbing solution.

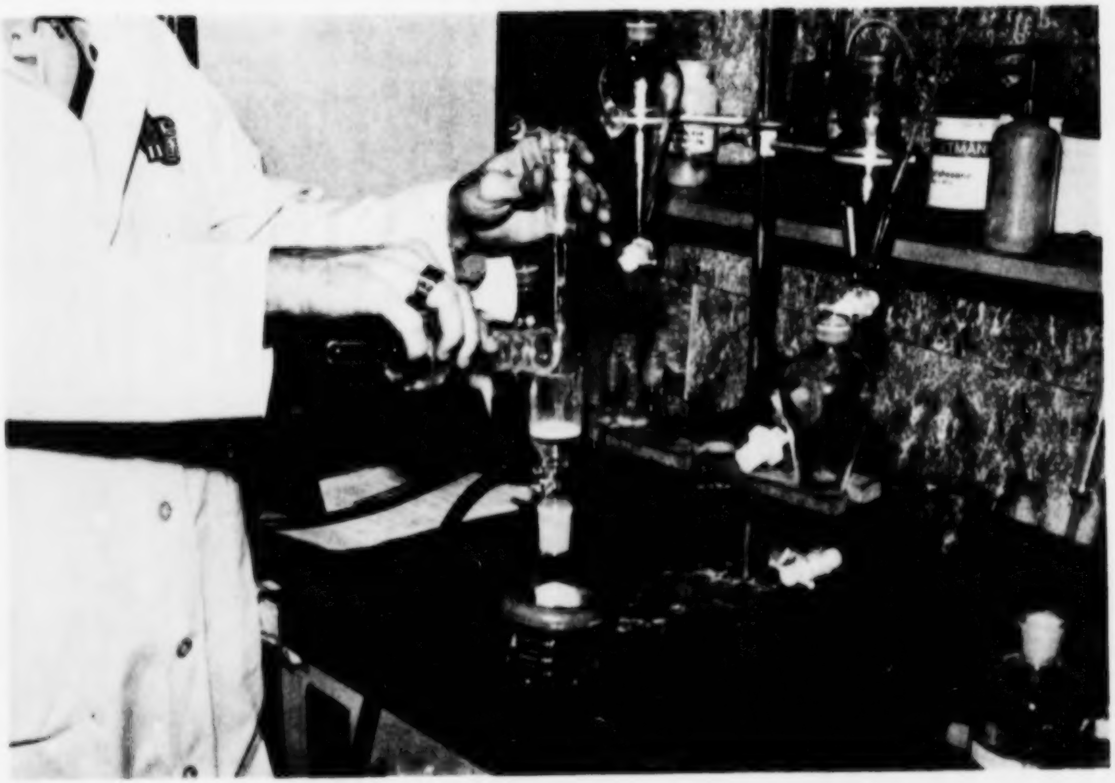


Figure 5. Filtration of absorbing solution.

traction step. The fritted glass filter containing the precipitate is connected to a dry flask. The two impingers that had previously contained the filtered precipitate are then each washed with small portions of methylene chloride. The methylene chloride dissolves any solid residue which was not removed by the water wash. These methylene chloride washings are poured into the fritted glass filter containing the precipitate. After the precipitate has been dissolved by the methylene chloride, a vacuum is applied to the flask and the methylene chloride solution is pulled through the filter into the flask. Another small amount of methylene chloride is poured through the filter into the flask to wash the filter. The methylene chloride solution is now saved until the extraction step is complete.

The extraction step is carried out as follows. The contents of the two impingers (if no precipitate is present) are transferred to a 250 mℓ separatory funnel. The impingers are each washed with small portions of deionized water which is also added to the separatory funnel. If a precipitate was found in the impingers the contents of the flask containing the filtered absorbing reagent and the water washings from the filtration step are transferred quantitatively to a 250 mℓ separatory funnel. The flask is washed with a small portion of water, and this water is added to the separatory funnel. Forty mℓ of pentane is now added to the separatory funnel containing the 80 mℓ of absorbing reagent and water washings. The funnel is stoppered and shaken for five minutes in an automatic shaker, Figure 6. The shaker is stopped and the funnel is vented. After the two phases are allowed to separate, the lower phase is collected in a second separatory funnel. The remaining phase is transferred to a third 250 mℓ separatory funnel. A second 40 mℓ portion of pentane is added to the already once extracted absorbing solution. The funnel is again stoppered, shaken for 5 minutes and vented. After the phases have separated, the lower phase is again collected in another separatory funnel. The upper or pentane layer is combined with the pentane layer from the first extraction. A third 40 mℓ portion of pentane is added to the twice extracted absorbing solution and the extraction process repeated. After the third extraction, the lower layer is discarded and the pentane layer is combined with the pentane layers from the first two extractions. Any absorbing solution which might have been accidently transferred with the pentane layers is drained off. Deionized water (25-50 mℓ) and sodium bicarbonate (1/4-1/2 gram) is added to the 250 mℓ separatory funnel containing the 120 mℓ of pentane extract. The funnel is stoppered and manually shaken for 30 seconds. The phases are allowed to separate and the lower water phase is drained off. Another 25 mℓ of deionized water is added and the shaking is repeated. After the phases have separated, the water is drained off insuring that all traces of water are removed. The contents of the funnel are then combined with the methylene chloride solution which was saved from the filtration step.

The flask containing the methylene chloride solution and the pentane extracts is then placed in a vacuum oven, Figure 7, operating at 50-60°C and 65" water vacuum until the pentane and methylene chloride have been removed. At this time only the dried phenylhydrazone derivative remain.

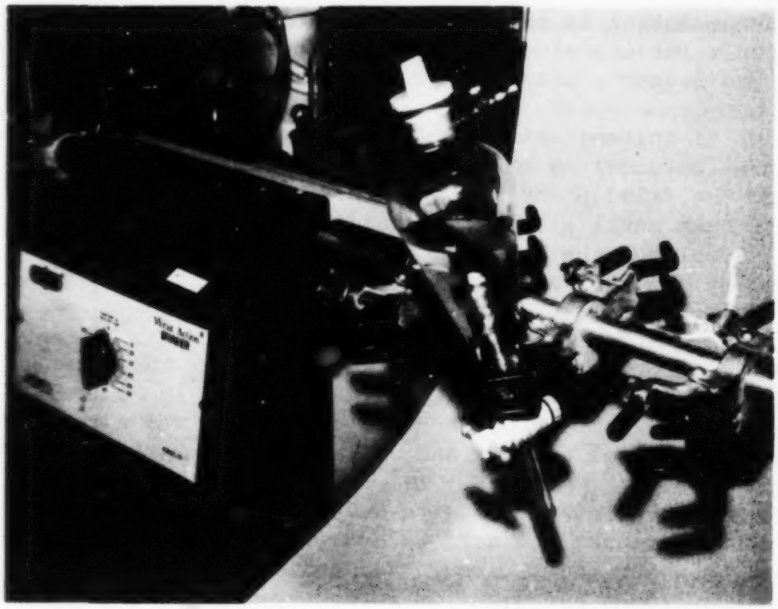


Figure 6. Automatic shaker.

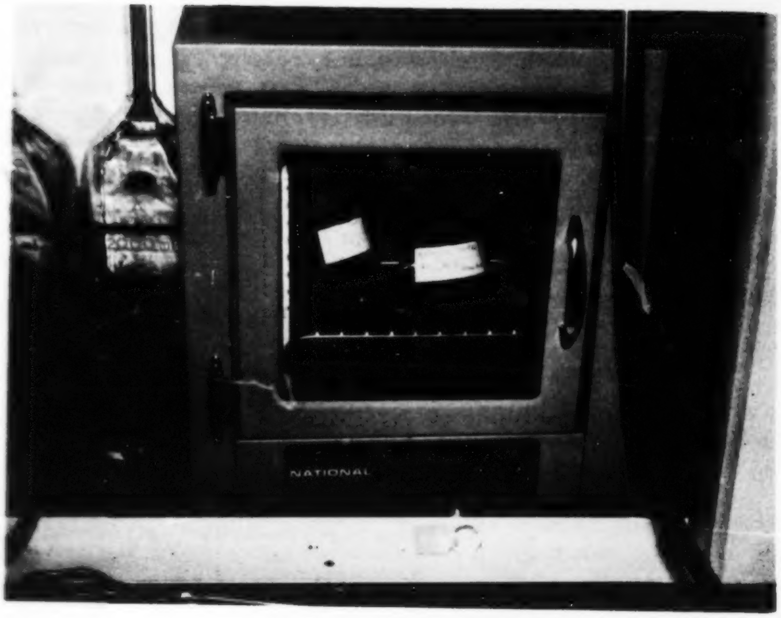


Figure 7. Vacuum oven.

Each time a series of samples are collected, a blank containing 80 mℓ of HCl/DNPH solution is extracted and dried in the same manner as the samples. This accounts for any aldehydes or interferring compounds which might be found in the reagents used for extraction.

Two mℓ of toluene which contain a quantitative amount of anthracene (∿0.05 mg/mℓ toluene) as an internal standard is pipetted into the flask containing the dried phenylhydrazone derivatives. The flask is then placed in a sonic bath until all of the residue is dissolved. After the precipitate has dissolved, the solution is transferred to a 1/2 dram vial (Figure 8). At this point the derivative is ready for injection into the gas chromatograph system.

The gas chromatograph system used to analyze the toluene solution containing the pherylhydrazone derivatives is shown in Figure 9. The system consists of a Varian 1700 GC, and A/D converter, and a recorder. The GC is equipped with dual columns and dual flame ionization detectors with a single differential amplifier. The columns consist of 24 x 1/8 inch O.D. stainless steel tubing packed with 6.7 percent Dexsil (polycarboranesiloxane) 300 GC on DMCS treated and acid washed, 60/80 mesh Chromosorb G. The carrier gas is helium which flows through the columns at a rate of 40 mℓ/minute. The optimum hydrogen and air flow rates are 35 mℓ/minute and 500 mℓ/minute, respectively. The column temperature, after injection of the sample, is programmed from 120°C to 300°C at 8° a minute. In a chromatogram of a standard sample (Figure 10) containing anthracene and the phenylhydrazone derivatives of formaldehyde, acetaldehyde, acetone, isobutryaldehyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde, the first peak eluted is toluene followed by anthracene, and then the derivatives of formaldehyde, acetaldehyde, acetone, isobutyraldhyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde. Data obtained from the five repetitive injections of the standard derivatives in toluene showed a maxsimum standard deviation of 4.56 percent for benzaldehyde and a minimum standard deviation of 0.87 percent for formaldehyde. The computer printout of the standard, Figure 10, is shown in Figure 11. This printout gives the retention time, area, and the name of each peak. The printout also gives the concentration of each of the derivatives in mg/mℓ. The concentration is calculated by the computer from response factors which are determined daily. Each day a standard containing known amounts of the derivatives and anthracene is injected into the GC. From the anthracene and derivative areas the computer calculates a response factor F. The F factors are used in all subsequent runs during the day to determine the concentration of the derivatives This response is calculated from the following equation:

$$\text{Response Factor (F)} = \frac{\text{Anthracene Area}}{\text{Derivative Area}} \times \frac{\text{mg/m}\ell\ \text{Derivative}}{\text{mg/m}\ell\ \text{Anthracene}}$$

Figure 8. 1/2 dram vials.

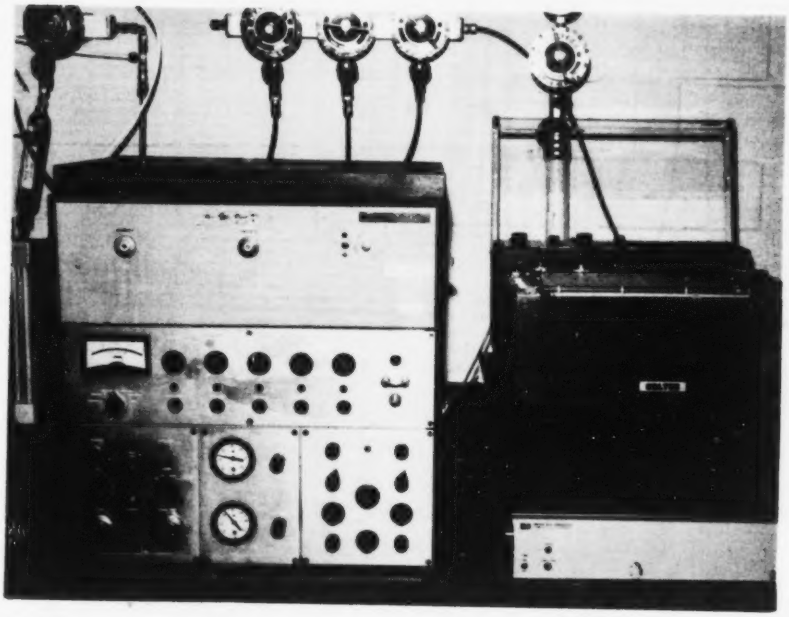
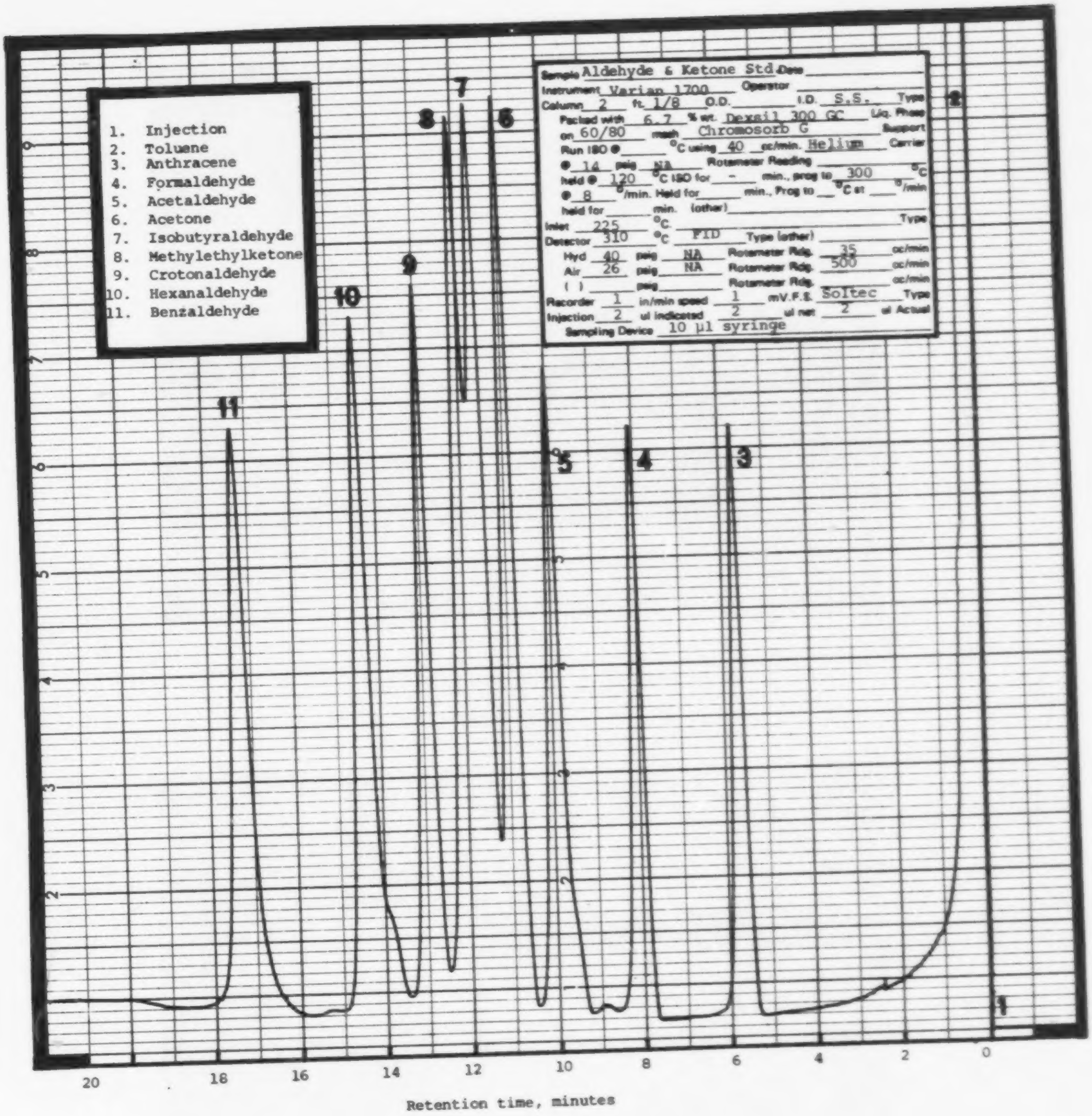


Figure 9. Aldehyde and ketone analytical system.



Sample Aldehyde & Ketone Std Date ____
Instrument Varian 1700 Operator ____
Column 2 ft. 1/8 O.D. ____ I.D. S.S. Type
Packed with 6.7 % wt. Dexsil 300 GC Liq. Phase
on 60/80 mesh Chromosorb G Support
Run ISO @ ____ °C using 40 cc/min. Helium Carrier
@ 14 psig NA Rotameter Reading ____
held @ 120 °C ISO for – min., prog to 300 °C
@ 8 °/min. Held for ____ min., Prog to ____ °C at ____ °/min
held for ____ min. (other) ____
Inlet 225 °C ____ Type
Detector 310 °C FID Type (other) ____
Hyd 40 psig NA Rotameter Rdg. 35 cc/min
Air 26 psig NA Rotameter Rdg. 500 cc/min
( ) ____ psig ____ Rotameter Rdg. ____ cc/min
Recorder 1 in/min speed 1 mV.F.S. Soltec Type
Injection 2 ul indicated 2 ul net 2 ul Actual
Sampling Device 10 µl syringe

Fiugre 10. Chromatogram of standard.

```
REPORT:    14.11  CHANNEL: 11

SAMPLE: STANDARD      INJECTED AT 11:18:27 ON MAR  1, 1978

ISTD METHOD: DNPH11


ACTUAL RUN TIME:  30.008 MINUTES

ISTD-RATIO:    .050,R MG/ML    STD-AMT:    .0500    SAMP-AMT:    1.0000


   RT        AREA        MG/ML         NAME

  7.26        9638 BB              &ANTHRACENE
  9.81       11159 BB     .203    #FORMALDEHYDE
 11.71       13355 BV     .202    #ACETALDEHYDE
 12.64       17898 VV     .203    #ACETONE
 13.28       16448 VV     .202    #ISO-BUTYRALDEHYDE
 13.70       16469 VV     .201    #MEK
 14.69       11167 VV     .199    #CROTONALDEHYDE
 16.08       15988 VV     .202    #HEXANALDEHYDE
 19.08       10525 BB     .198    #BENZALDEHYDE

TOTAL AREA =        122648        TOTAL MG/ML  =      1.610
```

Figure 11. Computer printout of standard.

Typical response factors for each of the derivatives are listed below:

Factor	Name
1.0000	Anthracene
3.1043	Formaldehyde
2.7736	Acetaldehyde
2.2366	Acetone
2.4160	Isobutyraldehyde
2.3332	Methylethylketone
3.4174	Crotonaldehyde
2.3428	Hexanaldehyde
2.9329	Benzaldehyde

When the response factor is known a concentration in mg/mℓ for each of the derivatives can be found. This concentration, along with the volume of sampled exhaust is then used to calculate the concentration of the carbonyl compounds in exhaust. Figures 12 and 13 show a typical sample chromatogram and accompanying printout respectively.

CALCULATIONS

This procedure has been developed to provide the user with the concentrations of the aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and ketones (acetone and methylethylketone) in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm for each carbonyl compound. The equations for determining the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F and pressure, 29.92"Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92"Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92"Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R)\ \ 29.92\text{" Hg}}$$

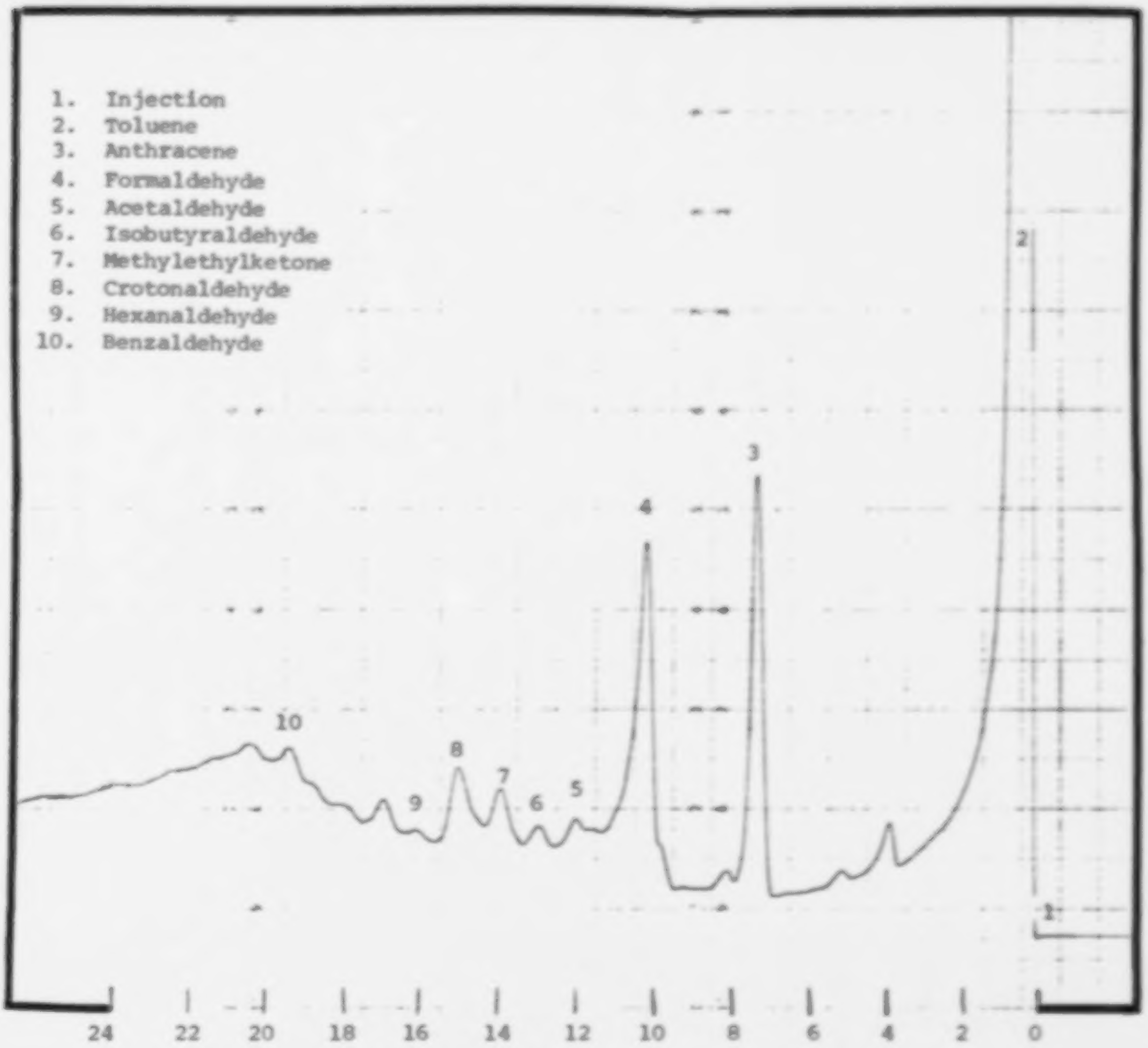


Figure 12. Sample chroamtogram.

```
REPORT:    20     CHANNEL: 11

SAMPLE: RC1             INJECTED AT  15:41:05 ON MAR  1, 1976

ISTD METHOD: DNPH11


ACTUAL RUN TIME:  30.017 MINUTES

ISTD-RATIO:     .050,R MG/ML    STD-AMT:      .0500    SAMP-AMT:     1.0000


  RT        AREA        MG/ML         NAME

  7.15        8604 BV              &ANTHRACENE
  7.95         435 VB     .003
 10.03        8877 BB     .186     #FORMALDEHYDE
 11.88         575 BV     .010     #ACETALDEHYDE
 12.83         463 VV     .007     #ISO-BUTYRALDEHYDE
 13.78        1594 VV     .022     #MEK
 14.85        2630 VV     .053     #CROTONALDEHYDE
 15.95         146 VV     .002     #HEXANALDEHYDE
 16.77         675 VV     .004
 19.20         648 VB     .012     #BENZALDEHYDE
 20.23        1912 BV     .011
 23.52         217 VV     .001
 25.03          13 VB 7.6E- 5
 25.48          84 BB 4.9E- 4

TOTAL AREA =         26874       TOTAL MG/ML =        .310

PROCESSED DATA FILE: *PRC11     RAW DATA FILE: *RAW11
```

Figure 13. Computer printout of sample.

The next step converts the volume from cubic feet to cubic meters by use of the conversion factor;1 cubic meter is equal to 35.31 cubic feet.

$$V_{\text{Corr}(m^3)} = \frac{P_{\text{exp}}\ (\text{"Hg}) \times V_{\text{exp}}\ (\text{ft}^3) \times 528°\text{R}}{T_{\text{exp}} \times 29.92\text{" Hg} \times 35.31\ \text{ft}^3/\text{m}^3}$$

(Equation 1)

The next step converts the mg/mℓ of derivative determined by the computer to mg of carbonyl collected in the two impingers. To obtain mg of derivative, the concentration (from the computer printout) in mg/mℓ is multiplied by the volume of toluene used to dissolve the solid extract.

$$\text{mg derivative} = \text{Conc}_{\text{Der}}(\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell)$$

To find mg of carbonyl compound per sample the mg of derivative are multiplied by the ratio of the molecular weight of the carbonyl derivative over the molecular weight of its phenylhydrazone derivative.

$$\text{mg carbonyl} = \text{mg derivative} \times \frac{\text{mol. wt. carbonyl}}{\text{mol. wt. derivative}}$$

$$= \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \frac{\text{mol. wt. carbonyl}}{\text{mol. wt. derivative}}$$

To obtain the number of µg of carbonyl compound the mg of carbonyl are multiplied by the conversion factor, 1000 µg/mg.

$$\mu\text{g carbonyl} = \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}(\text{m}\ell) \times \frac{\text{mol. wt. carbonyl}}{\text{mol. wt. derivative}} \times 1000\ \mu\text{g/mg}$$

(Equation 2)

The concentration of the carbonyl compound in exhaust can now be found in $\mu g/m^3$ by dividing equation 2 by equation 1.

$$\mu\text{g carbonyl/m}^3 = \frac{\text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \text{mol. wt. carbonyl}}{P_{\text{exp}}\ (\text{"Hg}) \times V_{\text{exp}}\ (\text{ft}^3) \times 528°} \times \frac{1000\ \mu\text{g/mg} \times T_{\text{exp}}\ (°\text{R}) \times 29.92\text{" Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{\text{mol. wt. derivative}}$$

(Equation 3)

To find the concentration of each carbonyl compound in ppm, the densities of carbonyls are needed. At 29.92" Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation.

$$\frac{V}{T} = \frac{V_1}{T_1}$$

$V_1 = 22.4$
$T_1 = 32°F + 460 = 492°R$
V = volume at 68°F
$T = 68°F + 460 = 528°R$

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04ℓ at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 24.04 ℓ/mole.

$$\text{den } (g/\ell) = \frac{\text{mol. wt. (g/mole)}}{24.04\ell/\text{mole}}$$

The density in µg/mℓ can be found by converting g to µg and µg and ℓ to mℓ as follows:

$$\text{den } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04\ell/\text{mole}} \times \frac{1 \times 10^6\ \mu g/g}{1 \times 10^3\ m\ell/\ell} \times \frac{\text{mol. wt.} \times 1000}{24.04}$$

(Equation 4)

To obtain the concentration of each carbonyl in ppm, the concentration in µg/m³ is divided by the density in µg/mℓ

$$\text{ppm} = \mu g/m^3 \div \mu g/m\ell = \frac{m\ell}{m^3}$$

Using Equations 3 and 4 gives the ppm concentration in the form of the raw data.

$$\text{ppm} = \frac{\text{Conc}_{\text{Der}}\ (mg/m\ell) \times \text{Vol}_{\text{Tol}}\ (m\ell) \times \text{mol. wt. carbonyl} \times 1000\ \mu g/m\ell}{P_{\text{exp}}\ (\text{"Hg}) \times V_{\text{exp}}\ (ft^3) \times 528° \times \text{mol. wt. derivative}}$$

$$\times \frac{T_{\text{exp}}\ (°R) \times 29.92\text{" Hg} \times 35.31\ ft^3/m^3 \times 24.04\ \ell/\text{mole}}{\text{mol. wt carbonyl} \times 1000}$$

$$= \frac{\text{Con}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times T_{\text{exp}}\ ({}^\circ\text{R}) \times 29.92''\ \text{Hg}}{P_{\text{exp}}\ (''\text{Hg}) \times V_{\text{exp}}\ (\text{ft}^3) \times 528^\circ}$$

$$\times \frac{35.31\ \text{ft}^3/\text{m}^3 \times 24.04\ \ell/\text{mole}}{\text{mol. wt. derivative}}$$

(Equation 5)

At this point, the concentration can be expressed in $\mu g/m^3$ (Equation 3) and ppm (Equation 5) at 68°F and 29.92" Hg from the raw data.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period a Hewlett-Packard 67 program was developed to calculate the aldehyde and ketone concentrations in $\mu g/m^3$ and ppm from the raw data and phenylhydrazone derivative concentrations (from computer printout). This program is presented in Figure 14.

Sample Calculations

Assume exhaust samples were collected in glass impingers for each portion of a three bag 1975 FTP. Raw data for these tests is presented in Figure 15. Calculations [illegible]rformed using the HP-67 programs and manual calculations.

Manual calculation for driving cycle FTP-1:

$$\mu g/m^3 \text{ formaldehyde} = \frac{\text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \text{mol. wt. carbonyl}}{P_{\text{exp}}\ (''\text{Hg}) \times V_{\text{exp}}\ (\text{ft}^3)}$$

$$\times \frac{1000\ \mu g/\text{mg} \times T_{\text{exp}}\ ({}^\circ\text{R}) \times 29.92''\ \text{Hg}}{528^\circ\text{R}}$$

$$\times \frac{35.31\ \text{ft}^3/\text{m}^3}{\text{mol. wt. derivative}}$$

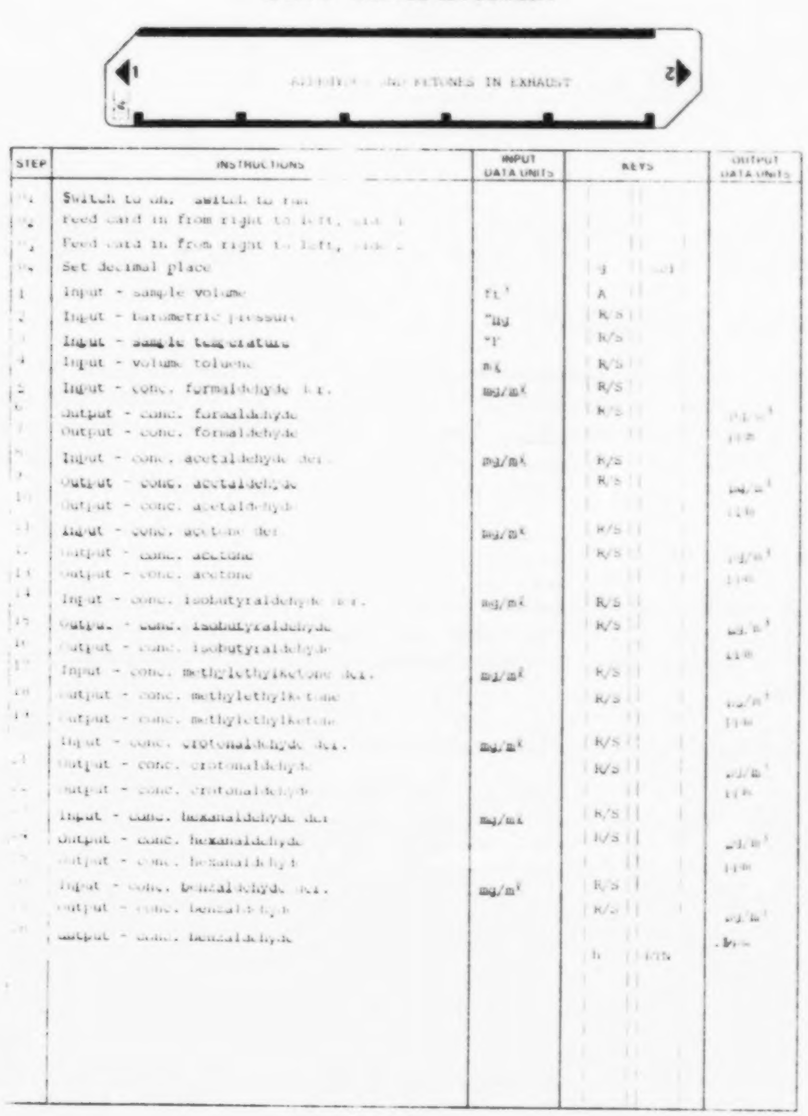
$$= \frac{0.186\ \text{mg/m}\ell \times 2\text{m}\ell \times 30.03\ \text{g/mole} \times 1000\ \mu g/\text{mg}}{29.80''\ \text{Hg} \times 3.196\ \text{ft}^3 \times 528^\circ\text{G}}$$

$$\times \frac{535^\circ\text{R} \times 29.92''\ \text{Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{201.15\ \text{g/mole}}$$

$$= 597.5\ \mu g/m^3$$

$$\text{ppm formaldehyde} = \mu g/m^3 \div \text{density}\ \mu g/\text{m}\ell$$

$$\text{density}\ \mu g/\text{m}\ell = \frac{\text{mol. wt. (formaldehyde)} \times 1000}{24.04\ell}$$

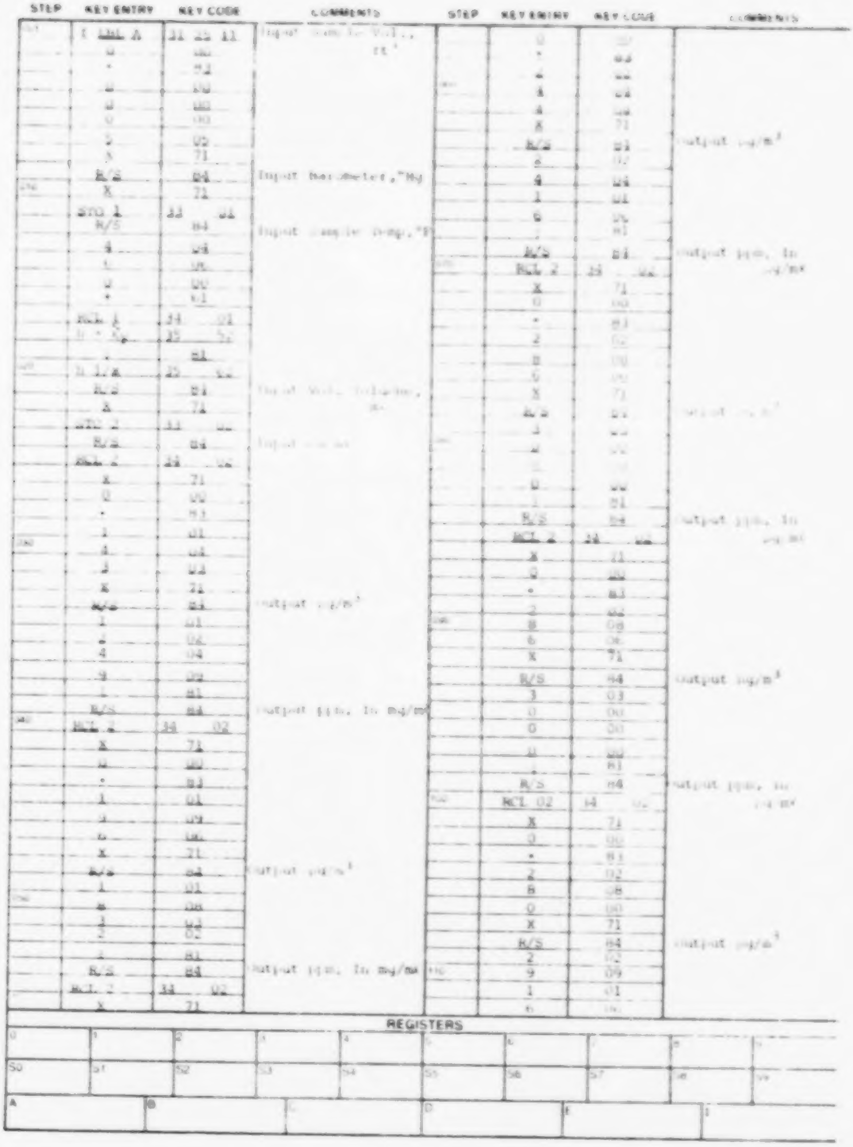


User Instructions

1 ALDEHYDES AND KETONES IN EXHAUST 2

STEP	INSTRUCTIONS	INPUT DATA UNITS	KEYS	OUTPUT DATA UNITS
01	Switch to on. switch to run			
02	Feed card in from right to left, side 1			
03	Feed card in from right to left, side 2			
04	Set decimal place		g [illegible]	
1	Input - sample volume	ft³	A	
2	Input - barometric pressure	"Hg	R/S	
3	Input - sample temperature	°F	R/S	
4	Input - volume toluene	mℓ	R/S	
5	Input - conc. formaldehyde der.	mg/mℓ	R/S	
6	Output - conc. formaldehyde		R/S	μg/m³
7	Output - conc. formaldehyde			ppm
8	Input - conc. acetaldehyde der.	mg/mℓ	R/S	
9	Output - conc. acetaldehyde		R/S	μg/m³
10	Output - conc. acetaldehyde			ppm
11	Input - conc. acetone der.	mg/mℓ	R/S	
12	Output - conc. acetone		R/S	μg/m³
13	Output - conc. acetone			ppm
14	Input - conc. isobutyraldehyde der.	mg/mℓ	R/S	
15	Output - conc. isobutyraldehyde		R/S	μg/m³
16	Output - conc. isobutyraldehyde			ppm
17	Input - conc. methylethylketone der.	mg/mℓ	R/S	
18	Output - conc. methylethylketone		R/S	μg/m³
19	Output - conc. methylethylketone			ppm
	Input - conc. crotonaldehyde der.	mg/mℓ	R/S	
21	Output - conc. crotonaldehyde		R/S	μg/m³
22	Output - conc. crotonaldehyde			ppm
23	Input - conc. hexanaldehyde der.	mg/mℓ	R/S	
24	Output - conc. hexanaldehyde		R/S	μg/m³
25	Output - conc. hexanaldehyde			ppm
26	Input - conc. benzaldehyde der.	mg/mℓ	R/S	
	Output - conc. benzaldehyde		R/S	μg/m³
28	Output - conc. benzaldehyde			ppm
			h RTN	

Figure 14. HP-67 user instructions.



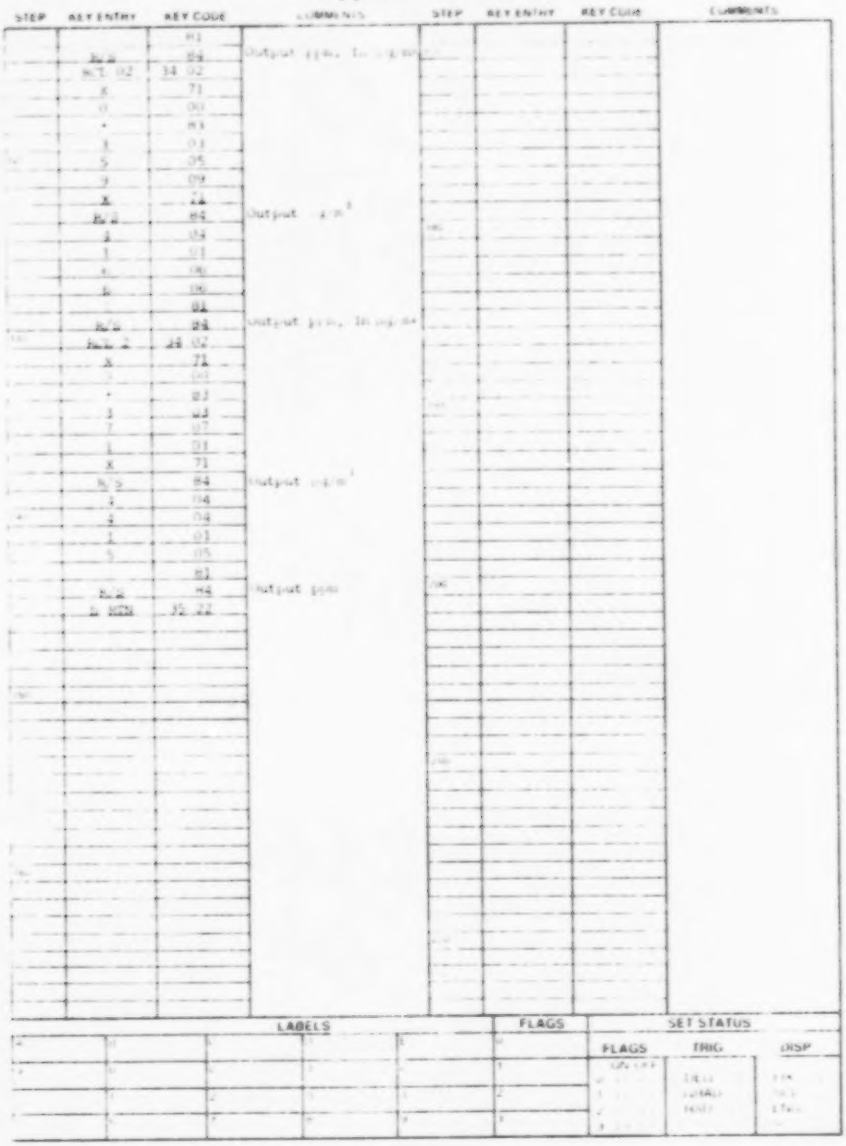
STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	Input Sample Vol., ft³
	0	00	
	.	83	
	0	00	
	0	00	
	0	00	
	5	05	
	X	71	
	R/S	84	Input Barometer, "Hg
010	X	71	
	STO 1	33 01	
	R/S	84	Input Sample Temp, °F
	4	04	
	6	06	
	0	00	
	+	61	
	RCL 1	34 01	
	h x⇄y	35 52	
	÷	81	
020	h 1/x	35 62	
	R/S	84	Input Vol. Collector, ml
	X	71	
	STO 2	33 02	
	R/S	84	Input [illegible]
	RCL 2	34 02	
	X	71	
	0	00	
	.	83	
	1	01	
030	4	04	
	3	03	
	X	71	
	R/S	84	Output μg/m³
	1	01	
	2	02	
	4	04	
	9	09	
	÷	81	
	R/S	84	Output ppm, In mg/m³
040	RCL 2	34 02	
	X	71	
	0	00	
	.	83	
	1	01	
	9	09	
	6	06	
	X	71	
	R/S	84	Output μg/m³
	1	01	
050	8	08	
	3	03	
	2	02	
	÷	81	
	R/S	84	Output ppm, In mg/m³
	RCL 2	34 02	
	X	71	

STEP	KEY ENTRY	KEY CODE	COMMENTS
	0	00	
	.	83	
	2	02	
060	4	04	
	4	04	
	X	71	
	R/S	84	Output μg/m³
	2	02	
	4	04	
	1	01	
	6	06	
	÷	81	
	R/S	84	Output ppm, In mg/m³
070	RCL 2	34 02	
	X	71	
	0	00	
	.	83	
	2	02	
	0	00	
	5	05	
	X	71	
	R/S	84	Output μg/m³
	1	01	
080	2	02	
	[illegible]	[illegible]	
	0	00	
	÷	81	
	R/S	84	Output ppm, In mg/m³
	RCL 2	34 02	
	X	71	
	0	00	
	.	83	
	2	02	
090	8	08	
	6	06	
	X	71	
	R/S	84	Output μg/m³
	3	03	
	0	00	
	0	00	
	0	00	
	÷	81	
	R/S	84	Output ppm, In mg/m³
100	RCL 02	34 02	
	X	71	
	0	00	
	.	83	
	2	02	
	8	08	
	0	00	
	X	71	
	R/S	84	Output μg/m³
	2	02	
110	9	09	
	1	01	
	6	06	

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9
A	B	C	D	E	I				

Figure 14 (Cont'd). HP-67 program form.



Program Listing

STEP	KEY ENTRY	KEY CODE	COMMENTS
	÷	81	
	R/S	84	Output ppm, In mg/m³
	RCL 02	34 02	
	×	71	
	0	00	
	.	83	
	1	01	
	5	05	
	9	09	
	×	71	
	R/S	84	Output mg/m³
	4	04	
	1	01	
	6	06	
	6	06	
	÷	81	
	R/S	84	Output ppm, In mg/m³
	RCL 2	34 02	
	×	71	
	0	00	
	.	83	
	1	01	
	7	07	
	1	01	
	×	71	
	R/S	84	Output mg/m³
	4	04	
	4	04	
	1	01	
	5	05	
	÷	81	
	R/S	84	Output ppm
	h RTN	35 22	

LABELS

FLAGS

SET STATUS

FLAGS

TRIG

DISP

Figure 14 (Cont'd). HP-67 program form.

SWRI PROJECT NO.________TEST NO.________TEST DATE:________VEHICLE:________
FUEL:______CVS NO.______TUNNEL SIZE:_______DRIVER:________MILES:________
SAMPLE COLLECTION BY:________CHEMICAL ANALYSIS BY:_____CALCULATIONS BY:______
GENERAL COMMENTS:____

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-2	FTP-3	SET-7	HFET	NYCC
Volume, Ft^3	3.196	1.625	2.010	3.730	8.241	1.070
B.P., "Hg	29.80	30.02	29.02	29.25	29.95	29.50
Temp. °F	75	80	96	85	83	89
Vol. Toluene ml	2	2	2	2	2	2
Formaldehyde Der Conc mg/ml	0.186	0.105	0.201	0.312	0.732	0.142
Formaldehyde Conc μg/m^3	598	665	1100	891	921	1410
Formaldehyde Conc ppm	0.479	0.532	0.881	0.713	0.737	1.130
Acetaldehyde Der Conc mg/ml	0.127	0.092	0.157	0.282	0.612	0.102
Acetaldehyde Conc μg/m^3	559	798	1170	1100	1060	1390
Acetaldehyde Conc ppm	0.305	0.436	0.639	0.600	0.579	0.759
Acetone Der Conc mg/ml	0.121	0.098	0.161	0.285	0.595	0.105
Acetone Conc μg/m^3	663	1060	1500	1390	1280	1780
Acetone Conc ppm	0.274	0.439	0.621	0.575	0.530	0.737
I-Bu Aldehyde Der Conc mg/ml	0.022	0.011	0.028	0.023	0.051	0.009
I-Bu Aldehyde Conc μg/m^3	141	139	305	131	128	179
I-Bu Aldehyde Conc ppm	0.047	0.046	0.102	0.044	0.043	0.060
MeEt Ketone Der Conc mg/ml	0.098	0.084	0.097	0.198	0.252	0.075
MeEt Ketone Conc μg/m^3	630	1060	1060	1130	634	1490
MeEt Ketone Conc ppm	0.210	0.353	0.353	0.377	0.211	0.497
Cro-Aldehyde Der Conc mg/ml	0.086	0.074	0.076	0.105	0.286	0.072
Cro-Aldehyde Conc μg/m^3	541	917	811	587	705	1400
Cro-Aldehyde Conc ppm	0.186	0.314	0.278	0.201	0.242	0.480
Hex-Aldehyde Der Conc mg/ml	0.031	0.018	0.030	0.027	0.078	0.011
Hex-Aldehyde Conc μg/m^3	250	286	411	194	246	275
Hex-Aldehyde Conc ppm	0.060	0.069	0.099	0.047	0.059	0.066
Benzaldehyde Der Conc mg/ml	0.093	0.081	0.097	0.121	0.232	0.081
Benzaldehyde Conc μg/m^3	775	1330	1370	897	757	2090
Benzaldehyde Conc ppm	0.176	0.301	0.310	0.203	0.171	0.473

Figure 15. Aldehyde collection sheet.

mol. wt formaldehyde = 30.03 g/mole

$$\text{density} = \frac{30.03 \text{ g/mole} \times 1000}{24.04\ell} = 1249\ \mu g/m\ell$$

$$\text{ppm} = 597.5\ \mu g/m^3 \div 1249\ \mu g/m\ell = 0.478\ m\ell/m^3 = 0.478 \text{ ppm}$$

The calculations for acetaldehyde, acetone, isobutyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde are carried out in the same manner by substituting the appropriate derivative concentrations and molecular weights into the above formulas. These calculations give the following concentrations:

acetaldehyde,	561 $\mu g/m^3$	and 0.306 ppm
acetone,	663 $\mu g/m^3$	and 0.274 ppm
isobutyraldehyde,	141 $\mu g/m^3$	and 0.047 ppm
methylethylketone,	630 $\mu g/m^3$	and 0.210 ppm
crotonaldehyde,	541 $\mu g/m^3$	and 0.186 ppm
hexanaldehyde,	250 $\mu g/m^3$	and 0.060 ppm
benzaldehyde,	775 $\mu g/m^3$	and 0.176 ppm

Note: The values used in these calculations are picked from a range of temperatures, derivative concentrations, etc. to validate the calculations and may not be representative of expected raw data. The calculations are presented to confirm the manual and HP-67 calculations give the same results. This was confirmed for six sets of calculations.

LIST OF EQUIPMENT

The equipment required for the analysis of aldehyde and ketones is divided into three groups: sample acquisition, sample preparation, and sample analysis. Manufacturer, stock number and any pertinent descriptive information are listed.

Sample Acquisition

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.

2. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/minute range.

3. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/minute.

4. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.

5. Regulating valve, Nupro 4MG, stainless steel.

6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" ID x 1/8" ID.

7. Teflon solenoid valve, The Fluorocarbon Company, Model DV2-144NCA1.

8. Drying tube, Analabs, Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.

9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.

10. Digital readout for dry gas meter.

11. Miscellaneous electrical switches, lights, wirings, etc.

12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

13. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.

14. Variable autotransformer, Staco Inc., Type 3PN 1010.

15. Heating sleeve wrapped with insulation and insulation tape.

16. Class A, 20 mℓ volumetric pipets.

17. Class A, 1000 mℓ volumetric flask.

18. Teflon coated stirring bar.

19. Hot plate-stirrer, Corning, PC-351.

20. Stainless steel heated filter assembly - 7 cm, Scott, capable of temperature to 204°C, includes 2 heaters, adjustable thermostat switch, stainless steel insulated covers and sample bypass solenoid valves.

21. Glass microfiber filter discs, Reeve Angel 934-AH, Whatman, 7 cm diameter.

22. Flexible, heavy insulation heating tape, Briskeat®, width-1/2 inch, length-48 inches.

23. Temperature Controller, Athena, 100-600°F.

24. Heated TFE Teflon hose, Technical Heaters Inc, 5' x 1/4", temperature limit 400°F.

Sample Preparation

1. Fritted glass filters, Ace Glass Company, porosity D, ASTM 10-20 microns pore size, 24/40 ground glass joint, vacuum takeoff.
2. Constant temperature vacuum oven, National Appliance Company.
3. Pump for oven, Thomas Industries, Model 907CA18 2.
4. Flasks, 125 mℓ capacity, 24/40 ground glass joints.
5. Separatory funnels, 125 mℓ.
6. Separatory funnels, 250 mℓ.
7. Separatory funnel shaker, Burrell Corporation, Wrist-Action® type with appropriate funnel holders, Model 75.
8. Ring stands, labels, holders, tubing, vacuum tubing, fittings and clamps needed for equipment manipulation.
9. Wash bottles, 500 mℓ.
10. Graduated cylinders, 50 mℓ.
11. Vials, Kimble, 1/2 dram.
12. Vacuum pump, Sargent-Welch.

Sample Analysis

1. Varian 1700 gas chromatograph equipped with dual flame ionization detectors in differential operation, and a linear temperature programmer.
2. Soltec Model B-281 1 mv recorder.
3. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout.
4. Syringe, 10 mℓ, Hamilton Company, #701.
5. Dual columns, 24 x 1/8" ID, stainless tubing packed with 6.7 percent Dexsil 300 GC on Chromosorb G 60/80 mesh, DMCS treated and acid washed.

LIST OF REAGENTS

A list of the reagents used in the determination of the aldehydes and ketones in exhaust is provided along with chemical formula, molecular weight, purity, manufacturer, and catalog number.

1. Hydrochloric acid, HCl, 36.46 g/mole, concentrated (37%), analytical reagent, Mallinckrodt, Cat. #2612.

2. Pentane, C_5H_{12}, 72.15 g/mole, Distilled in glass (bp 35-37°C), Burdick and Jackson Laboratories, Inc.

3. 2,4 Dinitrophenylhydrazine (2,4-DNPH), $(NO_2)_2C_6H_3CH{=}N{-}NH_2$, 210.149 g/mole, Aldrich analyzed, Aldrick, Cat. #D19,930-3.

4. Sodium Bicarbonate, $NaHCO_3$, 84.00 g/mole, Mallinckrodt, Cat. #7412.

5. Anthracene, $C_{14}H_{10}$, 178.24 g/mole, K and K Laboratories, Cat. #10714.

6. Toluene, $C_6H_5CH_3$, 92.14 g/mole Baker Analyzed Reagent, Baker Cat. #3-9460.

7. Methylene Chloride, CH_2Cl_2, 84.93 g/mole, Reagent ACS, Eastman, Cat. #13022.

PREPARATION OF ABSORBING SOLUTION

To prepare the absorbing solution, 163 mℓ of concentrated HCl and 2.5 g of 2,4-DNPH crystals are added to a one liter volumetric flask containing about 500 mℓ of deionized water. The flask is diluted to mark and stirred for several hours at room temperature with an automatic stirrer/Teflon coated stirring bar to dissolve the DNPH. Fresh absorbing solution is prepared daily as needed.

PREPARATION OF TOLUENE/ANTHRACENE SOLUTION

Toluene containing approximately 0.05 mg anthracene per mℓ of toluene is used to dissolve the dried phenylhydrazone extracts. This solution is made by adding 100 mg of anthracene to a two liter volumetric flask and diluting to mark with toluene.

PREPARATION OF PHENYLHYDRAZONE DERIVATIVES

In order to obtain response factors for each of the phenyhydrazone derivatives to anthracene, pure derivatives were prepared from their respective aldehydes and ketones. These derivatives were made by adding each of the carbonyl compounds separately to a 2 N HCl-DNPH solution. The resulting orange to red precipitates were filtered and dried. The derivatives were then recrystallized from hot absolute ethanal. The melting points for each of the derivatives were compared to literature values before use. A GC trace was also made on each of the derivatives to further check the purity.

PREPARATION OF STANDARD SOLUTION OF PHENYLHYDRAZONE DERIVATIVES AND ANTHRACENE

A standard containing the phenylhydrazone derivatives and anthracene in toluene is prepared to obtain a response factor of each of the derivatives to anthracene. The solution is made by dissolving weighed amounts of anthracene and each of the derivatives in a quantitative volume of toluene. These solutions contain 0.05 mg anthracene per mℓ of toluene and 0.2 mg of each derivative per mℓ of toluene.

REFERENCES

This procedure is taken from the procedure: "Oxygenated Compounds in Automobile Exhaust-Gas Chromatograph Procedure" by Fred Stump, ESRL, Environmental Protection Agency, Research Triangle Park, North Carolina.

APPENDIX B

TOTAL CYANIDE PROCEDURE

THE MEASUREMENT OF TOTAL CYANIDE IN EXHAUST

The measurement of total cyanide (hydrogen cyanide and cyanogen) in dilute exhaust is accomplished by bubbling exhaust through glass impingers containing a 1.0 N potassium hydroxide absorbing solution. The cyanide reacts with the potassium hydroxide to form a stable salt which remains in solution. Upon completion of the test, an aliquot of the absorbing solution is treated with monopotassium dihydrogen phosphate buffer and Chloramine-T. The reaction of cyanide and Chloramine-T in the presence of the buffer releases a gas, cyanogen chloride. For analysis, a portion of this cyanogen chloride gas is injected into a gas chromatograph equipped with an electron capture detector (ECD). External cyanide standards in 1.0 N potassium hydroxide are used to quantify the results. The detection limit for this procedure is less than 0.01 ppm.

SAMPLING SYSTEM

Two glass impingers in series, with each containing 25 mℓ of 1.0 N potassium hydroxide, are used to collect exhaust samples for analysis of cyanide. A flow schematic of the sample collection system is shown in Figure 1. The two glass impingers, when maintained at ice bath temperature (0-5°C), collect 99+ percent of the hydrogen cyanide and cyanogen. The flow rate through the impinger is maintained at 4 ℓ/minute by the sample pump. A dry gas meter is used to determine the total flow through the impinger during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A flowmeter in the system allows continuous monitoring of the sample flow. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. When sampling from diesel fueled vehicles, a heated filter, located between the on-off solenoid valve and the dilution tunnel, is used to prevent diesel particulate from contaminating the sampling system. The filter and line connecting the filter to the dilution tunnel are heated to 375°F in order to keep hydrogen cyanide and cyanogen from being retained on the removed particulate. The Teflon line connecting the heated filter and the solenoid valve is heated to ~175°F in order to prevent water from condensing in the sample line. Several views of the sampling system are shown in Figure 2.

ANALYTICAL PROCEDURE

The analysis of total cyanide (hydrogen cyanide and cyanogen) in exhaust is accomplished with the use of a gas chromatograph equipped with an electron capture detector (ECD). This detector is highly sensitive to halogens and

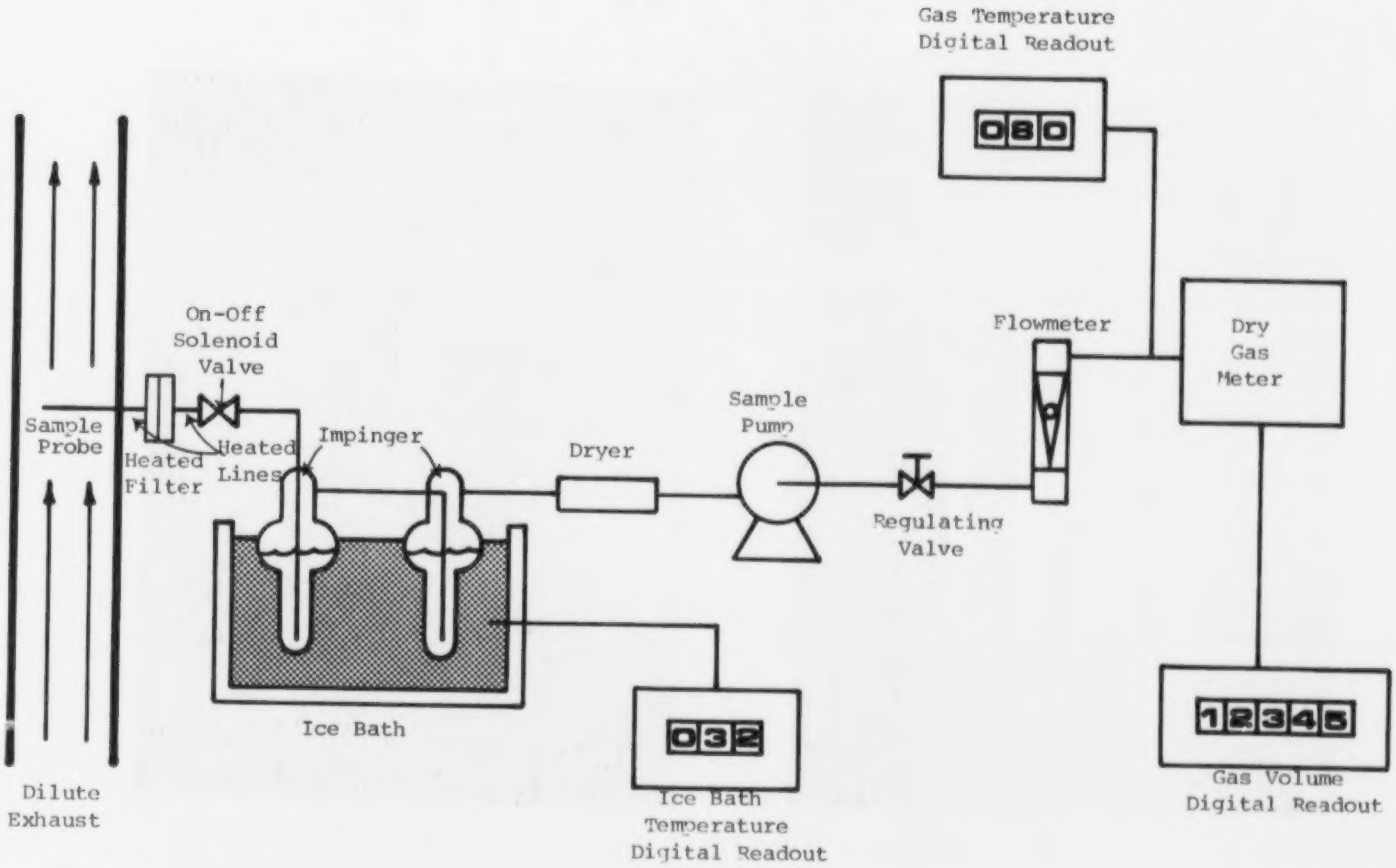
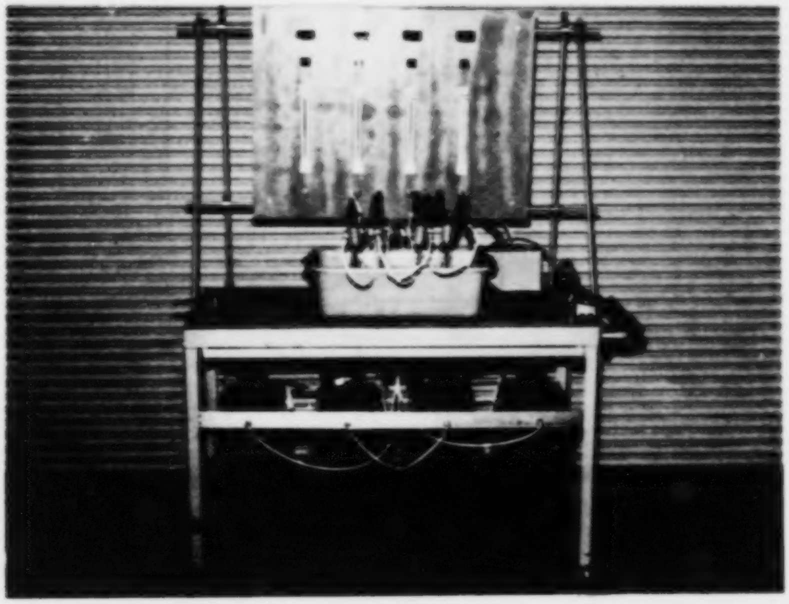
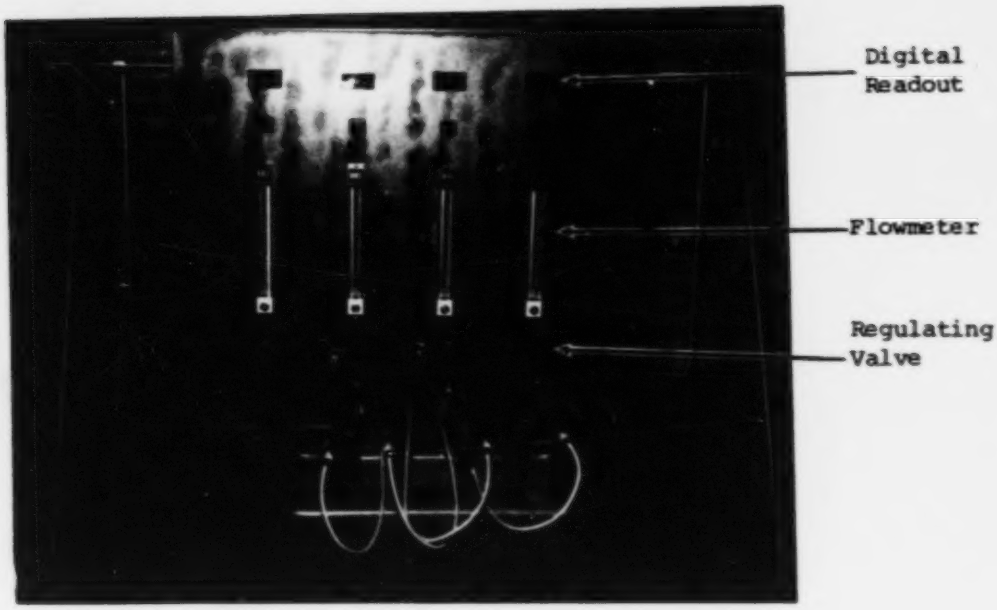

Gas Temperature
Digital Readout
080
On-Off
Solenoid
Valve
Flowmeter
Dry
Gas
Meter
Sample
Pump
Sample
Probe
Heated
Filter
Heated
Lines
Impinger
Dryer
Regulating
Valve
Ice Bath
032
Ice Bath
Temperature
Digital Readout
12345
Gas Volume
Digital Readout
Dilute
Exhaust

Figure 1. Total cyanide sample collection flow schematic.

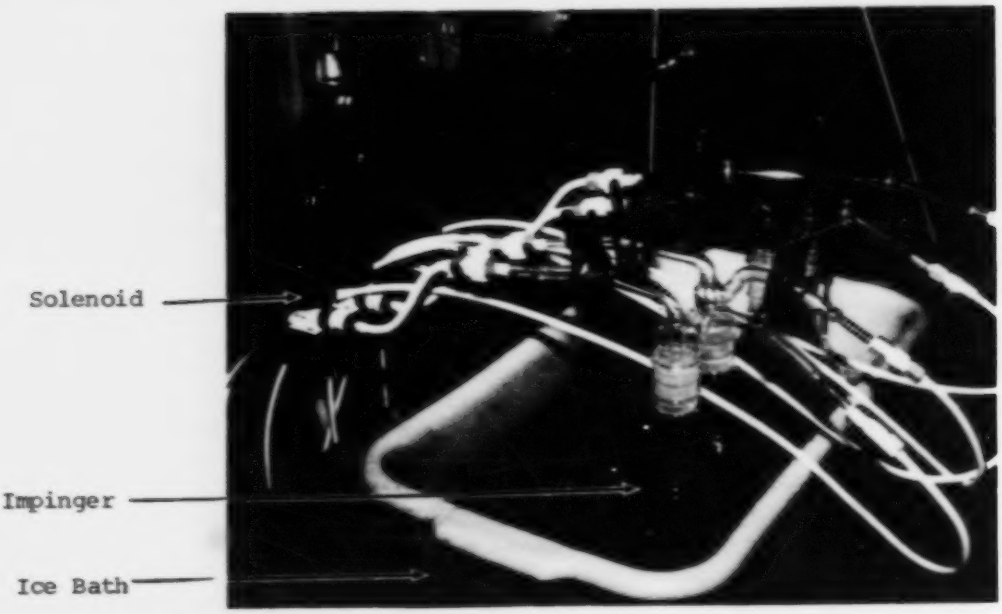


Front View

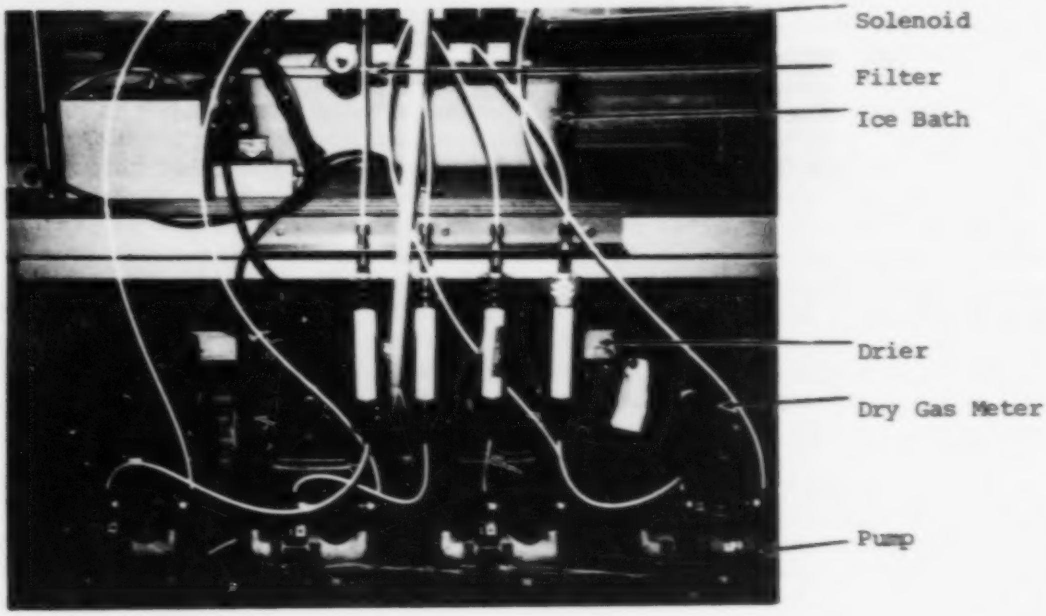

Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. Total cyanide sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). Total cyanide sampling system.

halogenated compounds. In this procedure the cyanide ion (CN^-) is reacted with Chloramine-T (sodium paratoluene sulfonchloramide) to form cyanogen chloride (CNCl) which can be detected at low concentrations by the ECD. Because of the sensitivity of the ECD to the halogenated cyanogen chloride, cyanide can be detected at low concentrations in exhaust by this procedure. A detailed description of this procedure follows. An analysis schematic for the procedure is shown in Figure 3.

During each test cycle a portion of the diluted exhaust is bubbled through two impingers in series, with each impinger containing 25 mℓ of 1.0 N potassium hydroxide. The temperature of the impingers is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4 ℓ/minute throughout the test cycle. Upon completion of each driving cycle, the impingers are removed and the content of each are transferred to a separate 30 mℓ ploypropylene bottle and capped. A 1 mℓ aliquot is removed from one of the bottles and placed in a 5 mℓ Glass Reacti-vial. A 2 mℓ aliquot of 1.0 N potassium dihydrogen phosphate buffer is then added carefully down the side of the vial. This adjusts the pH to neutral or slightly acid. A 1 mℓ aliquot of Chloramine-T is then carefully added down the side of the vial to the buffered solution. Turbulent addition of this reagent can cause premature release of cyanogen chloride. The cap with a septum top is immediately screwed tightly into place. The resulting solution is then set aside for 5 minutes. This allows the Chloramine-T to react completely with the trapped cyanide ion. The vial is then vibrated for 5 seconds to release cyanogen chloride into the gas phase. With a gas-tight syringe a 100 μℓ sample of the head space is removed through the septum top and immediately injected into the gas chromatograph. This procedure is then repeated for the second impinger. Some of the steps in this procedure are shown in Figure 4.

A Perkin-Elmer 3920B gas chromatograph with an ECD is used to analyze the sample. A 6' x 1/8" stainless steel column packed with 100/120 mesh Porapak Q is used to separate the cyanogen chloride from other compounds in the sample. The carrier gas, 95% argon-5% methane, flows through the column at a flow rate of 40 mℓ/minute. The column temperature is isothermal and maintained at 140°C. Oxygen, carbon dioxide, and water elude from the column before cyanogen chloride. The sample peak area is determined with a Hewlett-Packard Model 3354 computer system with a remote teletype printout. The peak area is compared to the peak area of a standard cyanide ion solution which is developed in a manner similar to that of the sample. Figure 5 shows the analytical system with gas chromatograph detector, integrator, and recorder.

This procedure provides a rapid and sensitive method for analyzing total cyanide in exhaust without extensive wet chemical work up. The analysis time is on the order of about 5 minutes after injection into the gas chromatograph. The sensitivity of the ECD extends the minimum detectable limit to less than 0.01 ppm cyanide ion with the specified flow rates, absorbing solution volume, syringe size, vial size, and reagent quantities. This limit can possibly be extended by changing these parameters. The simplicity and rapid data

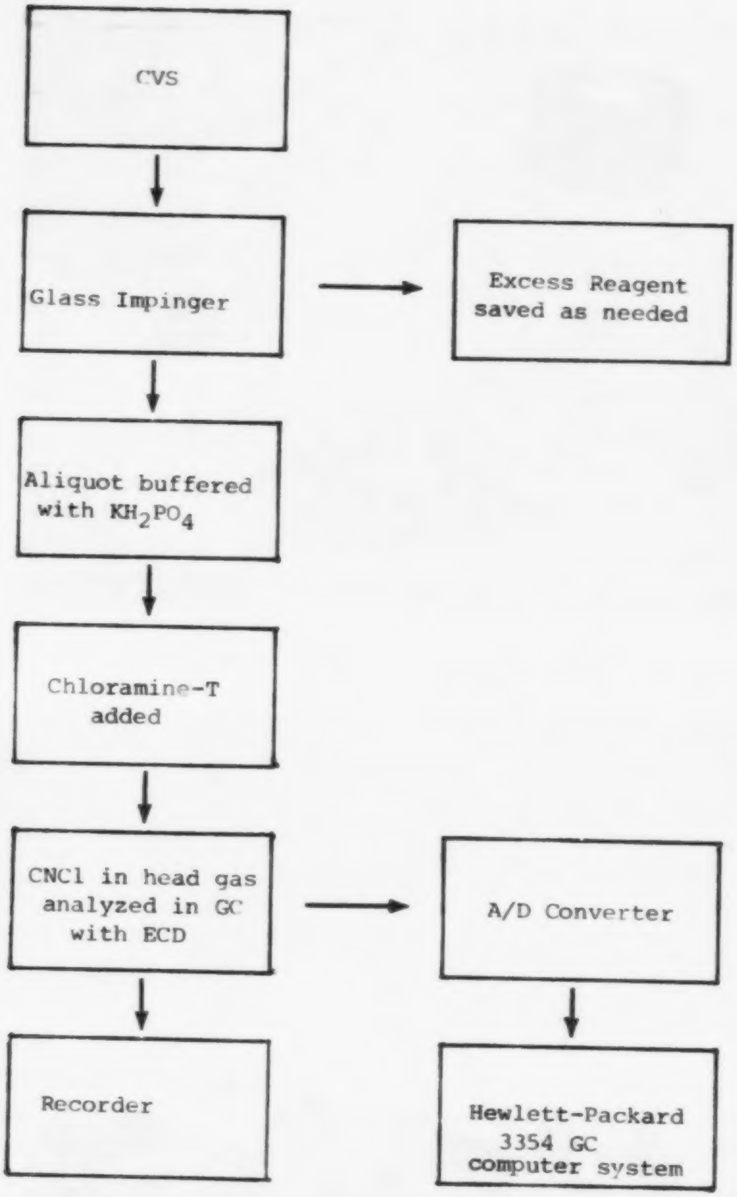
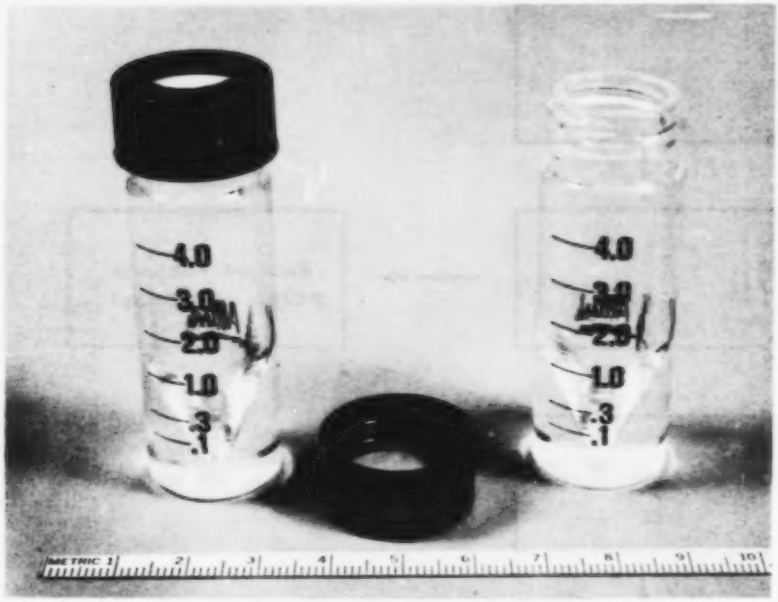
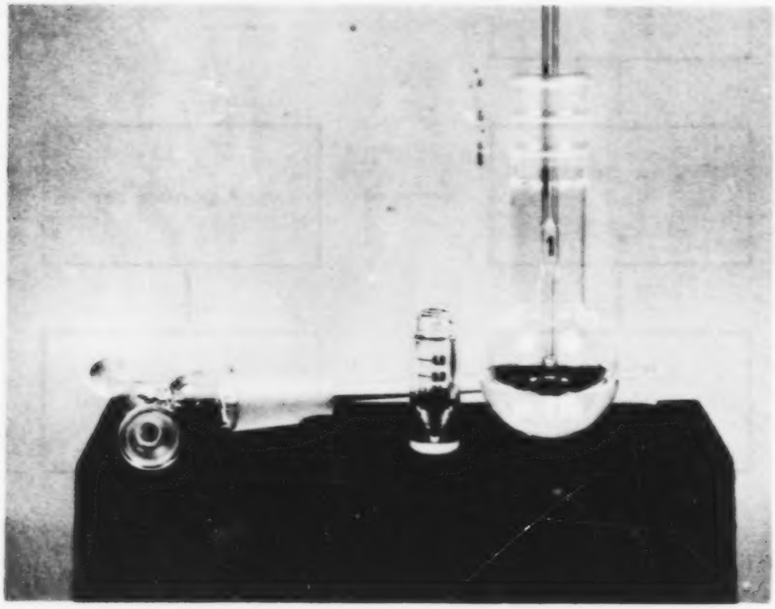

CVS
Glass Impinger
Excess Reagent saved as needed
Aliquot buffered with KH_2PO_4
Chloramine-T added
CNCl in head gas analyzed in GC with ECD
A/D Converter
Recorder
Hewlett-Packard 3354 GC computer system

Figure 3. Total cyanide (HCN + C_2H_2) analysis flow schematic.

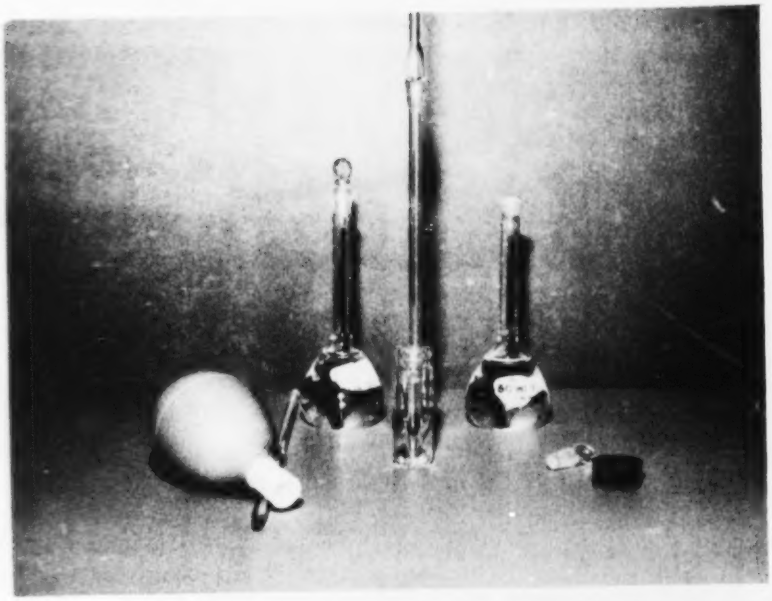

4.0
3.0
2.0
1.0
.3
.1
METRIC 1
2
3
4
5
6
7
8
9
10

Step 1. Glass reacti-vial with septum cap

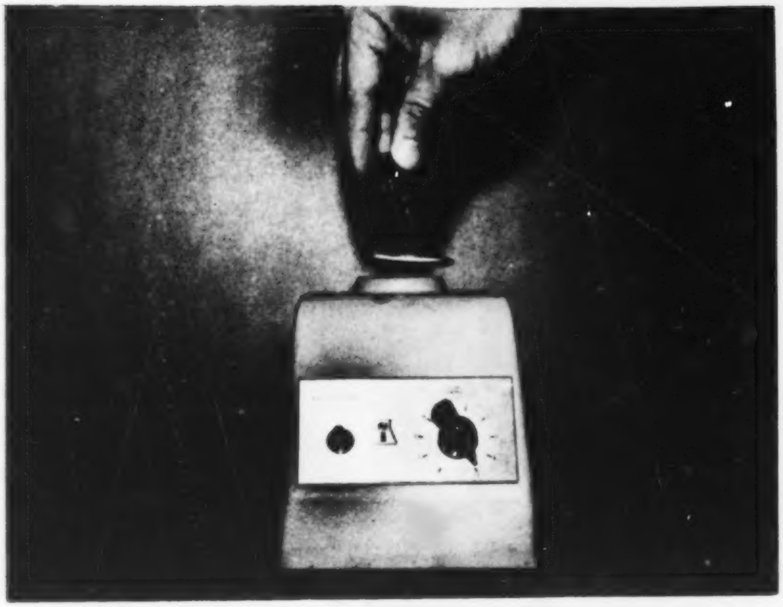


Step 2. Aliquot removal

Figure 4. Various steps in sample collection and analysis of total cyanide in exhaust.

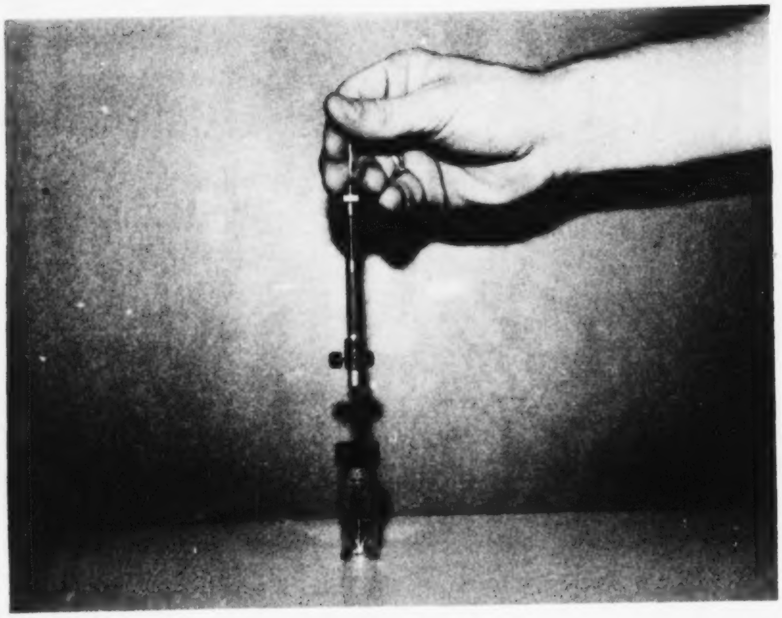


Step 3. Reagent addition

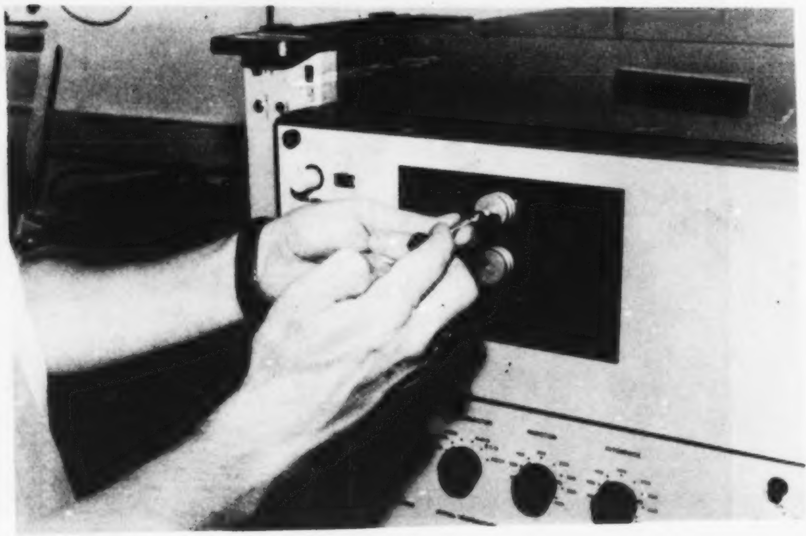


Step 4. Sample shaking

Figure 4 (Cont'd). Various steps in sample collection and analysis of total cyanide in exhaust.

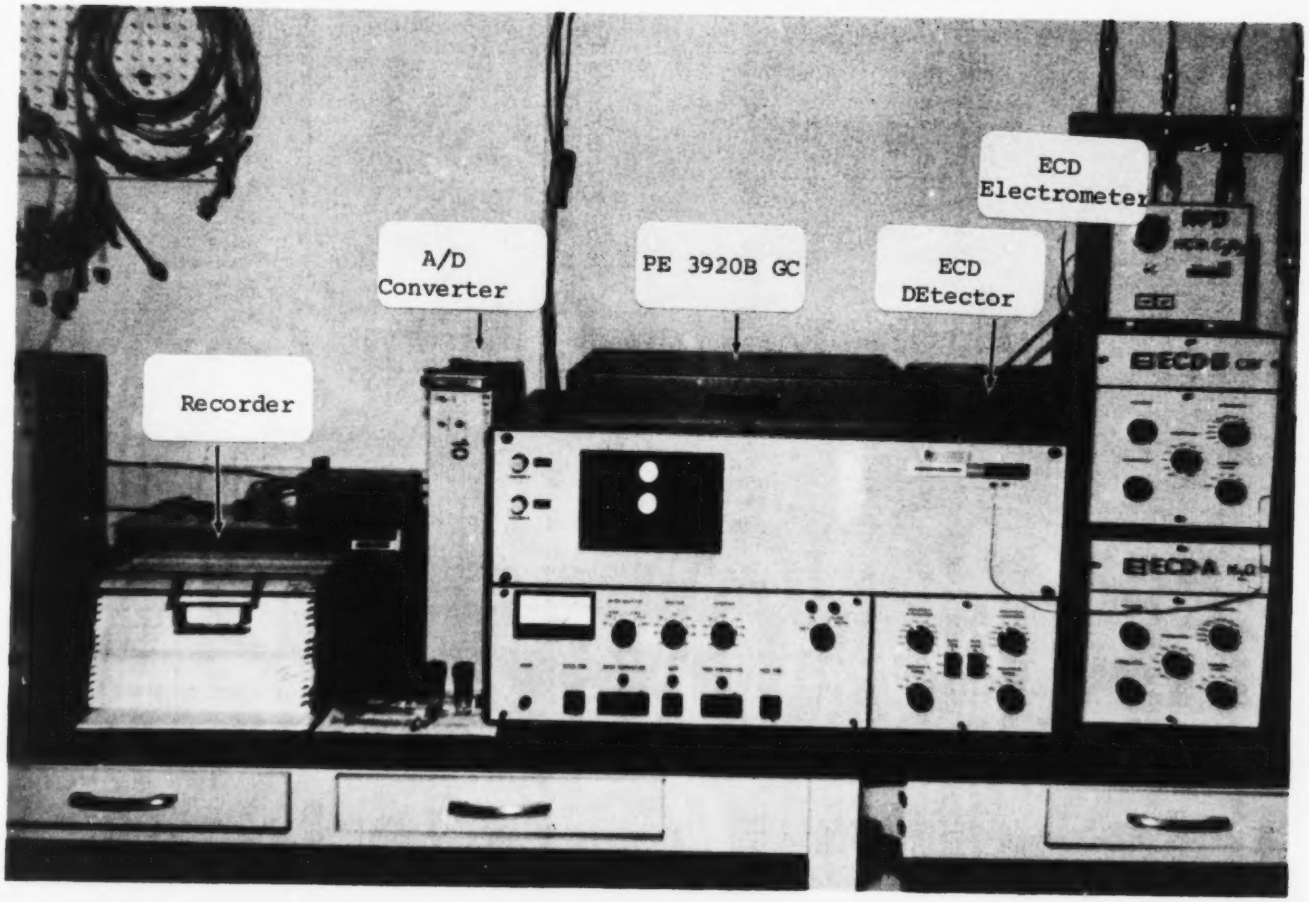


Step 5. Head gas removal



Step 6. Sample injection

Figure 4 (Cont'd). Various steps in sample collection and analysis of total cyanide in exhaust.


Recorder
A/D Converter
PE 3920B GC
ECD DEtector
ECD Electrometer

Fiugre 5. Total cyanide analytical system.

turnover makes this procedure ideal for repetitive analysis. A gas chromatograph trace for a cyanide standard is shown in Figure 6.

CALCULATIONS

This procedure has been developed to provide the user with the concentration of total cyanide in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm. The equations for determining the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92"Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92"Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92"Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{"Hg}}$$

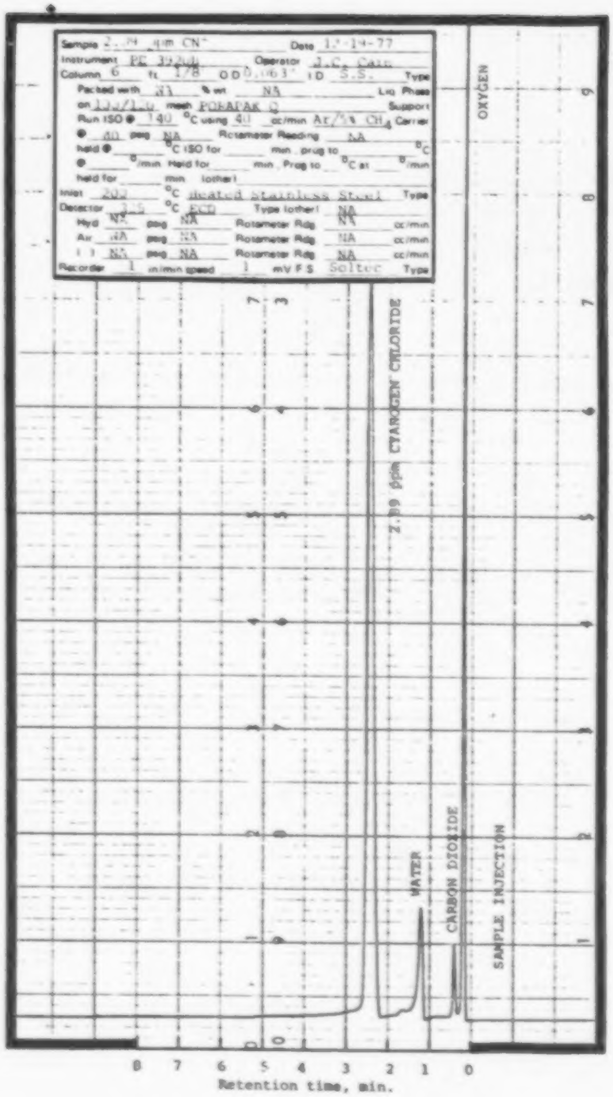
The next step converts the volume from cubic feet to cubic meters by use of the conversion factor; 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr}(m^3) = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}(ft^3) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)

The next step is to find the concentration of total cyanide in $\mu g/m\ell$. Since the gas chromatograph ECD has a linear response in the concentration of concern, then the following equation holds.

$$\frac{C_{sam}\ (\mu g/m\ell)}{A_{sam}} = \frac{C_{std}\ (\mu g/m\ell)}{A_{std}}$$



Sample 2.39 ppm CN⁻ Date 12-19-77
Instrument PE 3920B Operator J.C. Cain
Column 6 ft 1/8 OD 0.063" ID S.S. Type
Packed with NA % wt NA Liq Phase
on 100/120 mesh PORAPAK Q Support
Run ISO @ 140 °C using 40 cc/min Ar/5% CH_4 Carrier
@ 40 psig NA Rotameter Reading NA
held @ °C ISO for min, prog to °C
@ °/min Held for min, Prog to °C at °/min
held for min (other)
Inlet 200 °C Heated Stainless Steel Type
Detector 325 °C ECD Type (other) NA
Hyd NA psig NA Rotameter Rdg NA cc/min
Air NA psig NA Rotameter Rdg NA cc/min
( ) NA psig NA Rotameter Rdg NA cc/min
Recorder 1 in/min speed 1 mV F.S. Soltec Type

Figure 6. Typical trace for a standard.

C_{sam} = concentration of the sample in μg/mℓ
A_{sam} = GC peak area of sample in relative units
C_{std} = concentration of the standard in μg/mℓ
A_{std} = GC peak area of standard in relative units

Solving for C_{sam} gives:

$$C_{sam}\ (\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam}}{A_{std}}$$

The C_{sam} (μg/mℓ) in solution is corrected for any necessary dilution by multiplying by the dilution factor, D.F.

$$C_{sam}\ (\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F.}{A_{std}}$$

To obtain the total amount of μg of total cyanide in the absorbing solution, the absorbing reagent volume is multiplied by the concentration to give:

$$\mu g \text{ sample} = C_{sam}\ (\mu g/m\ell) \times \text{Abs. Vol. } (m\ell)$$
$$= \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F. \times \text{Abs. Vol. } (m\ell)}{A_{std}}$$

(Equation 2)

To obtain μg sample/m^3, Equation 2 is divided by Equation 1 to give:

$$\mu g \text{ sample}/m^3 = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F. \times \text{Abs. Vol. } (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg}) \times 528°}$$
$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ (ft^3/m^3)}{V_{exp}\ (ft^3)}$$

(Equation 3)

To find the concentration of total cyanide (as HCN) in ppm, the density of hydrogen cyanide is needed. At 29.92"Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation

$$\frac{V}{T} = \frac{V_1}{T_1}$$

V_1 = 22.4ℓ
T_1 = 32°F + 460 = 492°R
V = volume at 68°F
T = 68°F + 460 = 528°R

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04ℓ at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 22.04 ℓ/mole

$$\text{density } (g/\ell) = \frac{\text{mole. wt. g/mole}}{24.04\ \ell/\text{mole}}$$

The density in µg/mℓ can be found by converting g to µg and ℓ to mℓ as follows:

$$\text{density } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}} \times \frac{1 \times 10^6\ \mu g/g}{1 \times 10^3\ m\ell/\ell} = \frac{\text{mol. wt.} \times 1000}{24.04}$$

(Equation 4)

To obtain the concentration of total cyanide (as HCN) in ppm, the concentration in µg CN^-/m^3 needs to first be converted to µg HCN/m^3. This is done by multiplying the concentration in µg CN^-/m^3 by the ratio of the formula weight of HCN to the formula weight of CN^-.

$$\mu g\ HCN/m^3 = \mu g\ CN^-/m^3 \times \frac{\text{formula weight HCN } (\mu g/\mu \text{ mode})}{\text{formula weight } CN^- \ (\mu g/\mu \text{ mode})}$$

$$= \mu g\ CN^-/m^3 \times \frac{27.026\ \mu g\ HCN/\mu \text{ mole}}{26.018\ \mu g\ CN^-/\mu \text{ mole}}$$

$$= \mu g\ CN^-/m^3 \times 1.039\ \frac{\mu g\ HCN}{\mu g\ CN^-}$$

(Equation 5)

The concentration of total cyanide (as HCN) in ppm can now be obtained by dividing by the density in µg/mℓ.

$$\text{ppm (HCN)} = \mu g\ HCN/m^3 \div \text{density } \mu g/m\ell = m\ell/m^3$$

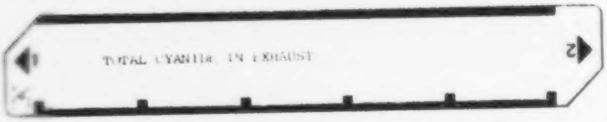
Using Equations 3, 4, and 5 gives the ppm concentration in the form of the raw data.

$$\text{ppm (HCN)} = \frac{24.04(\ell) \times C_{std}\ (\mu g\ CN^-/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{\text{mol. wt. (g/mole)} \times 1000 \times A_{std} \times P_{exp}\ (\text{"Hg})} \times \frac{T_{exp}\ (°R) \times 29.92\ \text{"Hg} \times 35.31\ ft^3/m^3 \times 1.039\ \frac{\mu g\ HCN}{\mu g\ CN^-}}{528°R \times V_{exp}\ (ft^3)}$$

(Equation 6)

At this point, the concentration can be expressed in µg CN^-/m^3 (Equation 3) and ppm (Equation 6) at 68°F and 29.92"Hg from the raw data.

User Instructions



STEP	INSTRUCTIONS	INPUT DATA UNITS	KEYS		OUTPUT DATA UNITS
0_1	Switch to on; switch to Run				
0_2	Feed Card in from right to left, side 1				
0_3	Set Decimal Place		g	SCI	
1	Input Sample Volume	ft^3	A		
2	Input Barometric Pressure	"Hg	R/S		
3	Input Sample Temperature	°F	R/S		
4	Input Absorbing Reagent Volume	mℓ	R/S		
5	Input Dilution Factor, Bubbler #1		R/S		
6	Input Standard Conc. Bubbler #1	µg CN$^-$/mℓ	R/S		
7	Input Standard Area, Bubbler #1	counts	R/S		
8	Input Sample Area, Bubbler #1	counts	R/S		
9	Output Sample Conc., Bubbler #1				µg CN$^-$/m^3
10	Input Dilution Factor, Bubbler #2		R/S		
11	Input Standard Conc., Bubbler #2	µg CN$^-$/mℓ	R/S		
12	Input Standard Area, Bubbler #2	counts	R/S		
13	Input Sample Area, Bubbler #2	counts	R/S		
14	Output Sample Conc., Bubbler #2		R/S		µg CN$^-$/m^3
15	Output Sample Conc., Bubbler #1 & #2		R/S		µg CN$^-$/m^3
16	Output Sample Conc.				ppm HCN
			h	RTN	

Fiugre 7. HP-65 user instructions.

STEP	KEY ENTRY	KEY CODE	COMMENTS	STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	In Sample Vol. ft^3				
	2	02					
	÷	81					
	R/S	84	In Barometric "Hg	060			
	X	71					
	STO 1	33 01					
	R/S	84	In Sample Temp. °F				
	4	04					
	6	06					
010	0	00					
	+	61					
	RCL 1	34 01					
	÷	81					
	R/S	84	In Sol. Vol., m^3	070			
	X	71					
	STO 2	33 02					
	RCL 2	34 02					
	R/S	84	In Dilution Factor				
	X	71					
020	R/S	84	In Std Conc $\mu g/m^3$				
	X	71					
	R/S	84	In Standard Area				
	÷	81					
	R/S	84	In Sample Area,	080			
	X	71	Bubbler #1				
	STO 3	33 03					
	R/S	84	Out Sam. Conc. Bubbler #1, $\mu g/m^3$				
	RCL 2	34 02	In Dilution Factor				
	X	71					
030	R/S	84	In Std Conc, $\mu g/m^3$				
	X	71					
	R/S	84	Input Std. Area				
	÷	81					
	R/S	84	In Sample Area,	090			
	X	71	Bubbler #2				
	R/S	84	Out Sam. Conc.				
	RCL 3	34 03	Bubbler #2, $\mu g/m^3$				
	+	61					
	R/S	84	Out Conc. $\mu g\ CN^-/m^3$				
040	1	01					
	.	83					
	0	00					
	3	03					
	8	08		100			
	7	07					
	X	71					
	1	01					
	1	01					
	2	02					
050	4	04					
	÷	81					
	R/S	84	Output ppm HCN				
	h RTN	35 22					
				110			

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A	B	C	D	E	I

Figure 7 (Cont'd). HP-65 program form.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period, a Hewlett-Packard 67 program was developed to calculate the total cyanide concentration in μg/m^3 and ppm from the raw data. This program is presented in Figure 7.

Sample Calculation

Assume exhaust samples were collected in glass impingers for each portion of a three-bag 1975 FTP. Raw data for these tests are presented in Fiugre 8. Calculations were performed using the HP-67 program and manual calculations.

Manual Calculations for Driving Cycle Cold-FTP

For Bubbler #1

$$\mu\text{g CN}^-/\text{m}^3 = \frac{C_{std}\ (\mu\text{g/m}\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. (m}\ell)}{A_{std} \times P_{exp}\ (\text{"Hg})}$$

$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{528°\text{R} \times V_{exp}\ (\text{ft}^3)}$$

$$= \frac{5.0\ \mu\text{g/m}\ell \times 1500 \times 1 \times 25\ \text{m}\ell}{2000 \times 29.19\text{"Hg}}$$

$$\times \frac{(460° + 70°) \times 29.92\text{"Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{528° \times 3.453\ \text{ft}^3}$$

$$= 986\ \mu\text{g CN}^-/\text{m}^3$$

The concentration in bubbler #2 is calculated in the same manner using the appropriate dilution factor, standard concentrations, standard area, and sample area:

For Bubbler #2

$$\mu\text{g CN}^-/\text{m}^3 = \frac{1\ \mu\text{g/m} \times 500 \times 1 \times 25\ \text{m}\ell}{1000 \times 29.19\text{"Hg}}$$

$$\times \frac{(460° + 70°) \times 29.92\text{"Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{528° \times 3.453\ \text{ft}^3}$$

$$= 131\ \mu\text{g CN}^-/\text{m}^3$$

SWRI PROJECT NO. 11-1234 TEST NO. 001 TEST DATE: 11-10-79 VEHICLE: Practice

FUEL: EM-237 CVS NO. 3 TUNNEL SIZE: 18" DRIVER: R.R. MILES: 1000

SAMPLE COLLECTION BY: D.E.B. CHEMICAL ANALYSIS BY: H.J.B. CALCULATIONS BY: L.R.S.

GENERAL COMMENTS:

Test No.	1	2	3	4	5	6
Driving Cycle	Cold FTP	Hot FTP	SET-7	HFET	NYCC	Background
Volume, Ft^3	3.453	3.486	3.508	1.926	1.525	15.826
B.P., "Hg	29.19	28.66	29.33	29.40	29.10	29.04
Temp. °F	70	75	80	85	90	77
Absorb. Rea. Vol., mℓ	25	25	50	50	25	25
Dilution Factor, Bubbler #1	1	5	10	2	1	1
Std. Conc $\mu gCN^-/m\ell$ Bub. #1	5	2	1	1	2	1
Std. Area - Bubbler #1	2000	1500	3000	5000	10,000	58
Sample Area - Bubbler #1	1500	1800	2500	4500	9000	4000
Sample Conc $\mu gCN^-/m^3$, Bub #1	986	3213	4374	1732	1115	2000
Dilution Factor, Bubbler #2	1	1	1	2	1	1
Std. Conc $\mu gCN^-/m\ell$ Bub. #2	1	1	2	0.5	1	0.5
Std. Area - Bubbler #2	1000	2000	3000	2000	3000	2000
Sample Area - Bubbler #2	500	1000	500	200	1900	500
Sample Conc $\mu gCN^-/m^3$, Bub#2	131	134	175	96	392	7
Total Conc. $\mu gCN^-/m^3$	1117	3347	4549	1829	1508	37
Total Conc. ppm HCN	1.03	3.09	4.20	1.69	1.39	0.03

Figure 8. Raw data sheet for total cyanide.

The concentrations from the two bubblers can be added for a total concentration:

$$\text{Total } \mu g\ CN^-/m^3 = \text{conc (bubbler \#1)} + \text{conc (bubbler \#2)}$$

$$= 986\ \mu g\ CN^-/m^3 + 131\ \mu g\ CN^-/m^3$$

$$= 1117\ \mu g\ CN^-/m^3$$

$$\text{ppm } CN^- \text{(as HCN)} = \mu g\ HCN/m^3 \div \text{density } \mu g/m\ell$$

$$\text{density } \mu g/m\ell = \frac{\text{Mol. Wt. (HCN)} \times 100}{24.04\ell}$$

Mol. Wt. HCN = 27.026 g/mole

$$\text{density } \mu g/m\ell = \frac{27.026 \times 100}{24.04} = 1124\ \mu g/m\ell$$

$$\mu g\ HCN/m^3 = \mu g\ CN^-/m^3 \times 1.039\ \mu g\ HCN/\mu g\ CN^-$$

$$= 1117 \times 1.039 = 1161$$

$$\text{ppm } CN^-\text{(HCN)} = 1161 \div 1124 = 1.03$$

Note: The values used in these calculations are picked from a range of temperatures, standards, dilution factors, etc. to validate the calculations and may not be representative of expected raw data in all cases. These calculations are presented to confirm that manual and HP-67 calculations give the same results. This was confirmed on six sets of calculations.

LIST OF EQUIPMENT

The equipment required in this analysis is divided into three basic categories: sample acquisition, sample preparation, and sample analysis. Manufacturer, stock number and any pertinent descriptive information are listed.

Sample Acquisition

1. Sample pump, Thomas model 106 CA18, capable of free flow capacity of 4 ℓ/minute.
2. Glass impingers, Ace Glass Products, catalog no. 7530-11 29/42 bottle joints, 18/7 arm joints
3. Flowmeter, Brooks Instrument Division, Model 1555, Tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/minute range.
4. Regulating valve, Nupro 4MG, stainless steel

5. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity

6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 1/8" ID

7. Teflon Solenoid Valve, The Fluorocarbon Company, Model DV2-144NCA1

8. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.

9. Drying tube, Nalgene Corporation, 10 cm length x 1/2 in. diameter

10. Digital readout for dry gas meter

11. Miscellaneous electrical switches, lights, wirings, etc.

12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

13. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation

14. Stainless steel heated filter assembly - 7 cm; Scott, capable of temperature to 204°C, includes 2 heaters, adjustable thermostat switch, stainless steel insulated covers and sample bypass solenoid valves

15. Glass microfiber filter discs, Reeve Angel 934-AH, Whatman, 7 cm diameter

16. Flexible heavy insulation heating tape, Briskeat®, width-1/2 inch, length-48 inches

17. Temperature Controller, Athena, 100-600°F

18. Heated TFE Teflon hose, Technical Heaters, Inc., 5' x 1/4", temperature limit 400°F.

Sample Preparation

1. Glass gas syringe, Teflon tipped plunger, 100 µl, Pressure-Lok Series A-2, Alltech Associates

2. Glass Reacti-vials, 5 mℓ, Pierce Chemical Company

3. Class A, 1 mℓ volumetric pipets

4. Class A, 2 mℓ volumetric pipets

5. Class A, 25 mℓ volumetric pipets

6. Class A, 50 mℓ volumetric flask

7. Class A, 100 mℓ volumetric flask

8. Class A, 250 mℓ volumetric flask

9. Class A, 500 mℓ volumetric flask

10. Class A, 1000 mℓ volumetric flask

11. Vortex-Genie, Scientific Industries, Inc. Model K-550-G

Instrumental Analysis

1. Perkin-Elmer Model 3920B gas chromatograph equipped with a linearized electron capture detector (ECD)

2. Soltec Model B-281 1 mv recorder

3. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout

LIST OF REAGENTS

This procedure requires the sample collection in glass impingers using a 1.0 N potassium hydroxide absorbing reagent. After collection, a buffer potassium phosphate monobasic is added to control the pH followed by Chlormaine-T to convert the CN^- to cyanogen chloride. Potassium cyanide is used as the CN^- standard in 1.0 N KOH. The reagents are listed below along with the manufacturer and quality.

1. Potassium phosphate monobasic, formula weight = 139.09, chemical formula = KH_2PO_4, ACS Analytical Reagent Grade, crystals, Mallinckrodt Code 7100.

2. Potassium hydroxide, formula weight = 56.11, chemical formula = KOH, ACS Analytical Reagent Grade, pellets, Mallinckrodt Code 6984

3. Potassium cyanide, formula weight = 65.12, chemical formula KCN, ACS Analytical Reagent Grade, granular, Mallinckrodt Code 6881

4. Chloramine-T (sodium para-toluene sulfonchloramide trihydrate), formula weight = 282.70, chemical formula = $p\text{-}CH_3C_6H_4SO_2NClNa \cdot 3H_2O$, Assay (by titration) 96% minumum, Eastman, crystals, Eastman Code 1022

PREPARATION OF REAGENTS

Primary Standard - the primary standard is prepared by dissolving 0.602 grams of KCN in 500 mℓ of 1.0 N KOH. This is equivalent to 500 ppm HCN (500 μg HCN/mℓ) or a 481 ppm CN^- (481 μg CN^-/mℓ). Additional standards are prepared from the primary standard. A typical dilution to prepare a 0-10 μg CN^-/mℓ calibration curve is as follows:

mℓ of 481 μg CN^-/mℓ Primary Standard	Final Diluent Volume, mℓ	CN^- concentration, μg/CN^-/mℓ
1.000 mℓ	50.0 mℓ	9.62
4.000 mℓ	250.0 mℓ	7.70
1.000 mℓ	100.0 mℓ	4.81
3.000 mℓ	500.0 mℓ	2.89
1.000 mℓ	250.0 mℓ	1.92
1.000 mℓ	500.0 mℓ	0.96

Buffer Solution - A 1.0 M KH_2PO_4 buffer solution is prepared by dissolving 13.609 g KH_2PO_4 in 100 mℓ of deionized H_2O. The buffer solution should be prepared daily.

Absorbing Reagent - The absorbing reagent is a 1.0 N KOH solution. This solution is prepared by dissolving 56.11 grams of KOH in 1000 mℓ of deionized water.

Chlormaine-T - The Chlormaine-T converts the CN^- to CNCl. This reagent is prepared by dissolving 250 mg in 100 mℓ of deionized water. This reagent is the most critical in this procedure and should be prepared daily.

REFERENCES

Braker, W. and Mossman, A.L., Matheson Gas Data Book, 5th Edition, East Rutherford, N.J., 1971, pg. 301

Epstein, J., Anal, Chem., Vol. 19, pg. 272, 1947

Collins, P.F., Sarji, N.M., and Williams, J.F., Tobacco Sci., Vol. 14, pg. 12, 1971

Collins, P.F., Sarji, N.M., and Williams, J.F., Breitrage zur Tabakforschung, Vol. 7, pg. 73, 1973

Sekerka, I. and Lechner, J.F., Water Res., Vol. 10, pg. 479, 1976

Ito, C., Sakamoto, H. and Kashima, T., Kyoritsu Yakko Daigaku Kenkyu Nempo, Vol. 18, pg. 29, 1973

Frant, M.S., Ross Jr., J.W., and Riseman, J.H., Anal. Chem., Vol. 44 pg. 2227, 1972

Riseman, J.H., Am. Lab., Vol. 4, pg. 63, 1972

Fleet, B., and von Storp, H., Anal. Chem, Vol. 43, pg. 1575, 1971

Fleet, B., and von Storp, H., Anal. Lett., Vol. 4, pg. 425, 1971

Conrad, F.J., Talanta, Vol. 18, pg. 952, 1971

Vickroy, D.G., and Gaunt Jr., G.L., Tabacco Sci., Vol. 174, pg. 50, 1972

Burke, James, "Ion Selective Electrode-Direct Technique, "Ford Motor Company procedure for measuring HCN in dilute automotive exhaust, 1976

Llenado, R.A. and Rechnitz, G.A., Anal. Chem., Vol. 43, pg. 1437, 1971

Nebergal, W.H., Schmidt, F.C., and Holtzclaw Jr., H.F., College Chemistry with Qualitative Analysis, 5th edition, D.H. Heath and Co., Lexington, Mass., 1976, pg. 684

Woolmington, K.G., J. Appl. Chem., Vol. 11, pg. 114, 1961

Isbell, R.E., Anal. Chem., Vol. 35, pg. 255, 1963

Myerson, A.L. and Chludzinski Jr., J.J., J. Chromatog. Sci., Vol. 13, pg. 554, 1975

Valentour,J.C., Aggarwal, V., and Sunshine, I., Anal. Chem., Vol. 46, pg. 924, 1974

Runge, H., Z. Anal. Chem., Vol. 189, pg. 111, 1962

APPENDIX C

INDIVIDUAL HYDROCARBON PROCEDURE

THE MEASUREMENT OF INDIVIDUAL HYDROCARBONS IN EXHAUST

This procedure was developed to measure individual hydrocarbons in dilute automotive exhaust. The term, individual hydrocarbons (IHC) is used to define the collection of compounds: methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2), propane (C_3H_8), propylene (C_3H_6), benzene (C_6H_6), and toluene (C_7H_8). Dilute exhaust is collected in Tedlar bags during a test cycle and analyzed with a gas chromatographic system containing four separate columns and a flame ionization detector (FID). The peak areas are compared to an external calibration blend and individual hydrocarbon concentrations are analyzed with a Hewlett-Packard 3354 computer system. The analysis flow schematic is shown in Figure 1.

ANALYTICAL SYSTEM

The analysis for individual hydrocarbons is conducted with a Varian Aerograph Series 1400 gas chromatograph using a flame ionization detector (FID). Four separate packed columns are used to resolve these individual compounds. An elaborate system of timers, solenoid valves, and gas sampling valves are used to direct the flow of the sample through the system. The actual analytical system is shown in Figure 2.

The first two columns are used to resolve air, methane, ethylene, ethane, acetylene, propane and propylene, respectively; while columns III and IV resolve benzene and toluene. Column I consists of an 8' x 1/8" stainless steel tube packed with Porapak Q 80/100 mesh. This column is primarily used to resolve methane from air. It undergoes temperature programming from 25°C to 100°C at 12°/min. Column II consists of a 4' x 1/8" Teflon column packed with 35/60 mesh type 58 Silica gel. C_2 and C_3 hydrocarbons are resolved with this column. It is held isothermal at room temperature (20°C). The third column is used to resolve benzene from the other aromatics, paraffins, olefins, and acetylenes. It consists of a 15' x 1/8" stainless steel column packed with 15 percent 1, 2, 3-tris (2-cyanoethoxy) propane on 60/80 mesh Chromosorb PAW. This column is held isothermal at 100°C at the end of the temperature program sequence. Column IV is a 2' x 1/8" stainless steel tube packed with 40 percent mercury sulfate ($HgSO_4$) and 20 percent sulfuric acid (H_2SO_4) on Chromosorb W. This column resolves benzene and toluene from the oxygenated hydrocarbons such as aldehydes and ketones. It is also held isothermal at room temperature for the entire analysis sequence. All samples pass through a 6' x 0.01" capillary restrictor before entering the detector. Helium is the carrier gas with a column flow of 52 mℓ/minute.

The temperature program sequence is accomplished with the oven of the

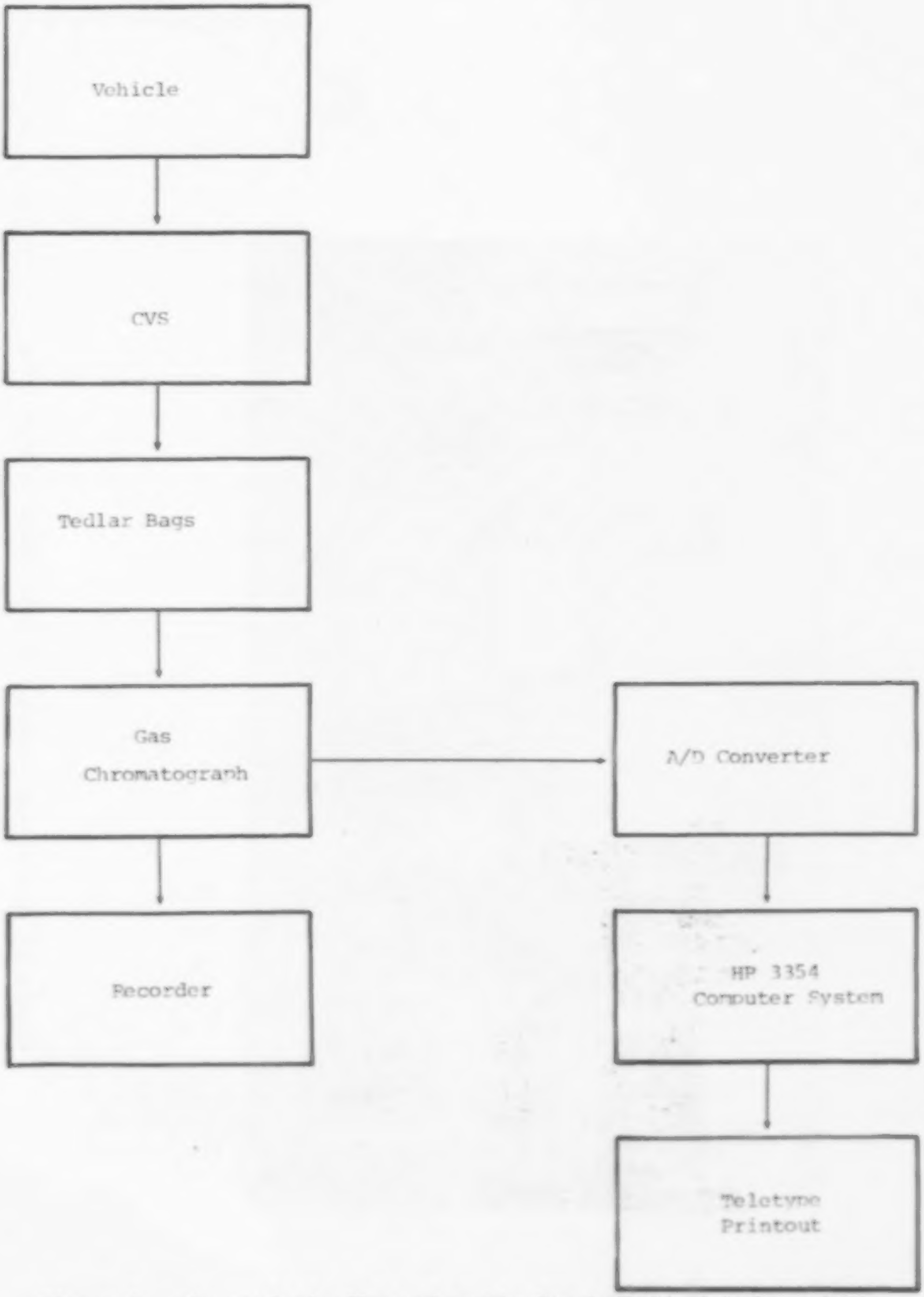

Vehicle
CVS
Tedlar Bags
Gas Chromatograph
Recorder
A/D Converter
HP 3354 Computer System
Teletype Printout

Figure 1. The analysis flow schematic for individual hydrocarbons.

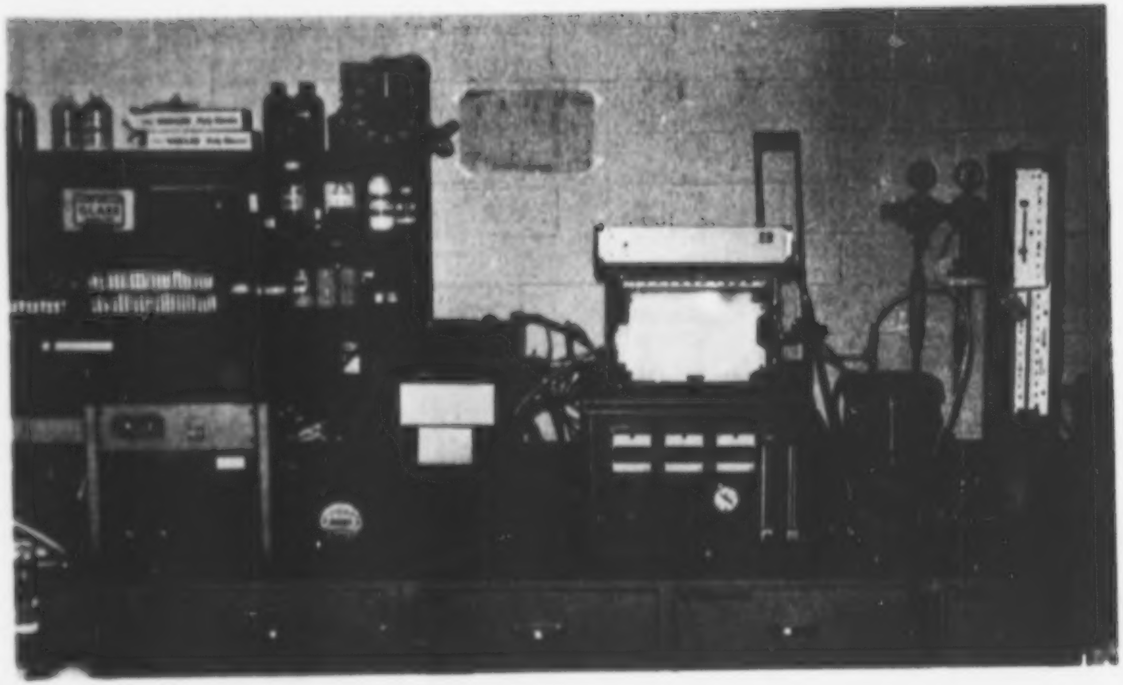


Figure 2. Analytical system for individual hydrocarbons.

gas chromatograph. Columns I and III are in this oven although Column I is the only one used during the temperature program. The gas sampling valves are contained in a Bendix Valve Oven. The temperature is maintained at 100°C. Columns II and IV are external to this oven for isothermal room temperature operation.

Samples as well as backgrounds are collected in Tedlar bags during the driving cycle. The sample is purged through two 10 mℓ sample loops for four (4) minutes. Samples from diesel fueled vehicles are passed through an ice trap before entering the sample loops. The ice trap removes high molecular weight compounds that can interfere with later analyses. The ice trap consists of 8 feet of 1/4 inch stainless steel tubing submerged in an ice bath. The initial configuration of the analytical system is shown in Figure 3. Upon injection, gas sampling valve A is activated by solenoid valve G, the temperature program sequence is started, and the first timer begins to count 680 seconds. The temperature program sequence for Columns I and II starts at 25°C and increases at 12°/min to a final temperature of 100°C. Columns I and III are held isothermal at this temperature for the remainder of the analysis. The configuration of the analytical system is shown in Figure 4. The sample in the first loop passes through Columns I and II and into the detector. The peaks (in the order of elution) are air, methane, ethylene, ethane, acetylene, propane and propylene. After 670 seconds, the second step begins with solenoid H activating gas sampling valve B. The second timer begins to count down 120 seconds. At this time, the sample trapped in the second 10 mℓ sample loop is channeled through Column III. The analytical system configuration is shown in Figure 5. After 120 seconds, step 3 begins. The third timer starts counting down 480 seconds and gas sampling valves C and J are activated by solenoid valve E. Columns I and II are backflushed through a capillary restrictor to the vent and Columns III and IV are directed to the detector. The configuration is shown in Figure 6. After 480 seconds, solenoid valve F activates gas sampling valve D. Column III is backflushed through a capillary restrictor to the vent. The final configuration is shown in Figure 7. The last two peaks in the order of elution are benzene and toluene. Upon elution of the last peak, the system is reset to the initial position.

A time/temperature system operation sequence is presented in Figure 8. The solid line on this graph represents the gas chromatograph oven temperature during the temperature program sequence. The time at which each step begins is also represented on the graph.

Figures 9 through 13 illustrate a simplified version of the flow of the carrier gas and sample through the gas sampling valves. Figure 9 shows the configuration of the gas sampling valves in the sample loop purge position. The sample is pumped out of the sample bag and through the sample loops. Column III is flushing and Column IV is backflushing to the vent and Columns I and II are directed to the detector. At the start of an injection, the position of gas sampling valve A changes and the trapped sample is directed to Columns I and II. Columns III and IV remain in the flushing mode. Figure 10 illustrates the analytical configuration upon injection. Step 2 begins with the

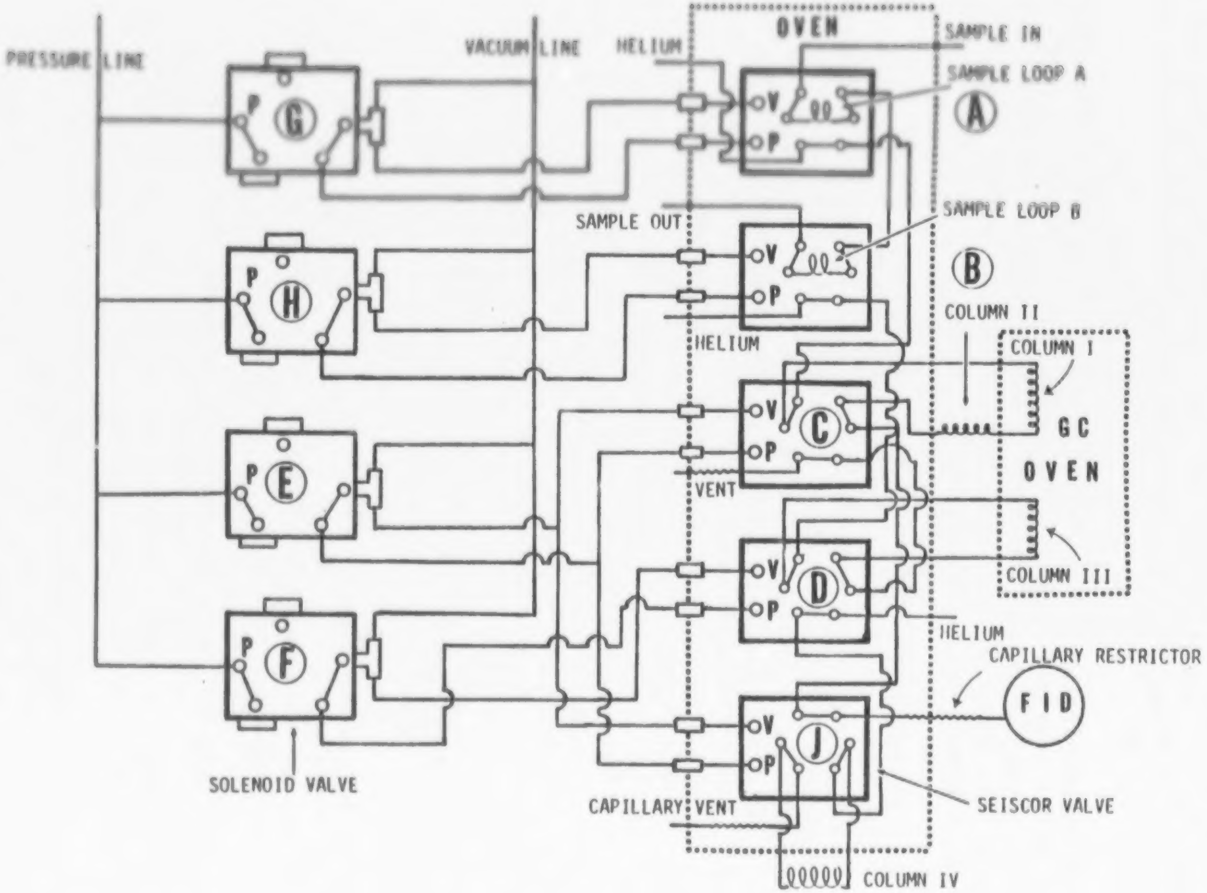

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
V
P
G
SAMPLE OUT
SAMPLE LOOP B
B
H
HELIUM
COLUMN II
COLUMN I
GC
OVEN
C
VENT
E
COLUMN III
D
HELIUM
CAPILLARY RESTRICTOR
FID
F
J
SOLENOID VALVE
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV

Figure 3. Initial analytical system configuration.

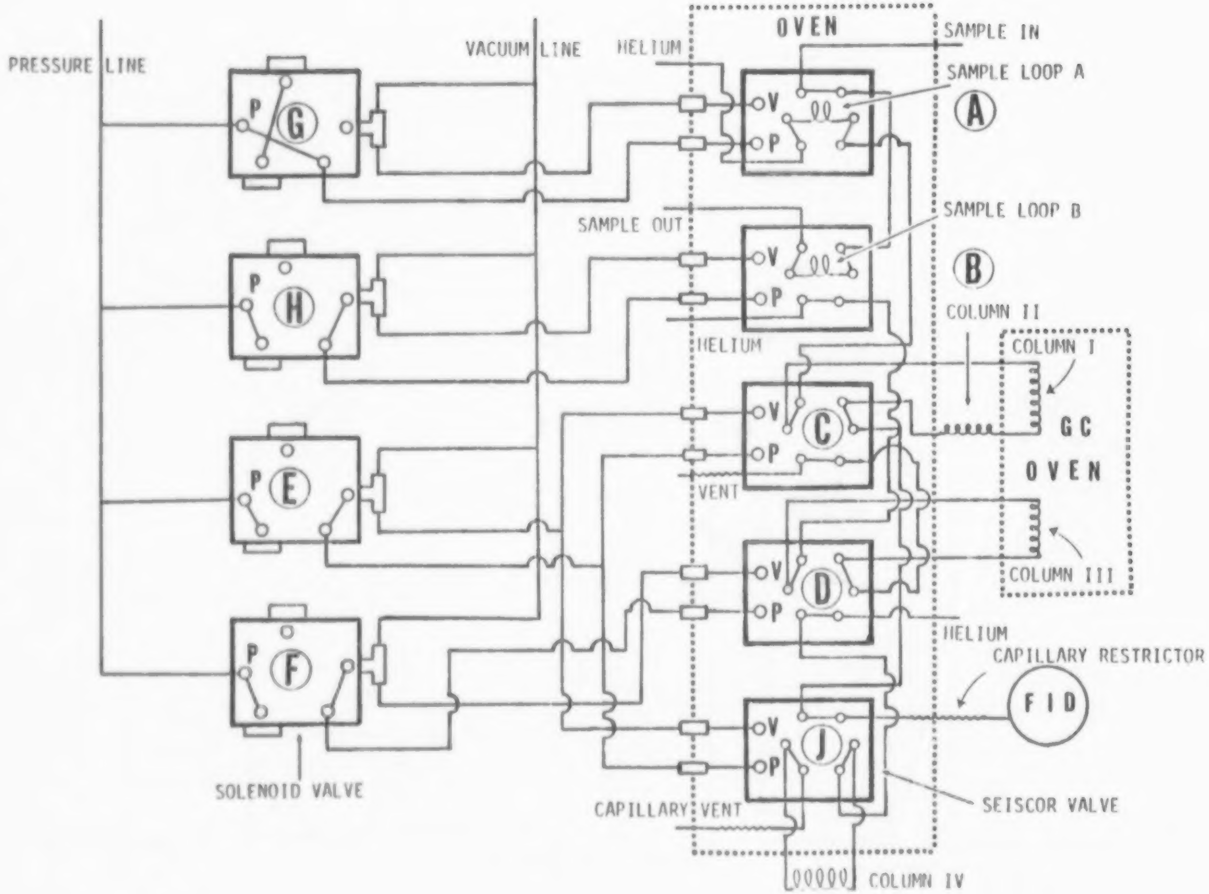

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
SAMPLE OUT
SAMPLE LOOP B
B
HELIUM
COLUMN II
COLUMN I
GC
OVEN
VENT
COLUMN III
HELIUM
CAPILLARY RESTRICTOR
FID
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV
SOLENOID VALVE
G
H
E
F
C
D
J
P
V

Figure 4. Step 1 solenoid G activation of gas sampling valve A.

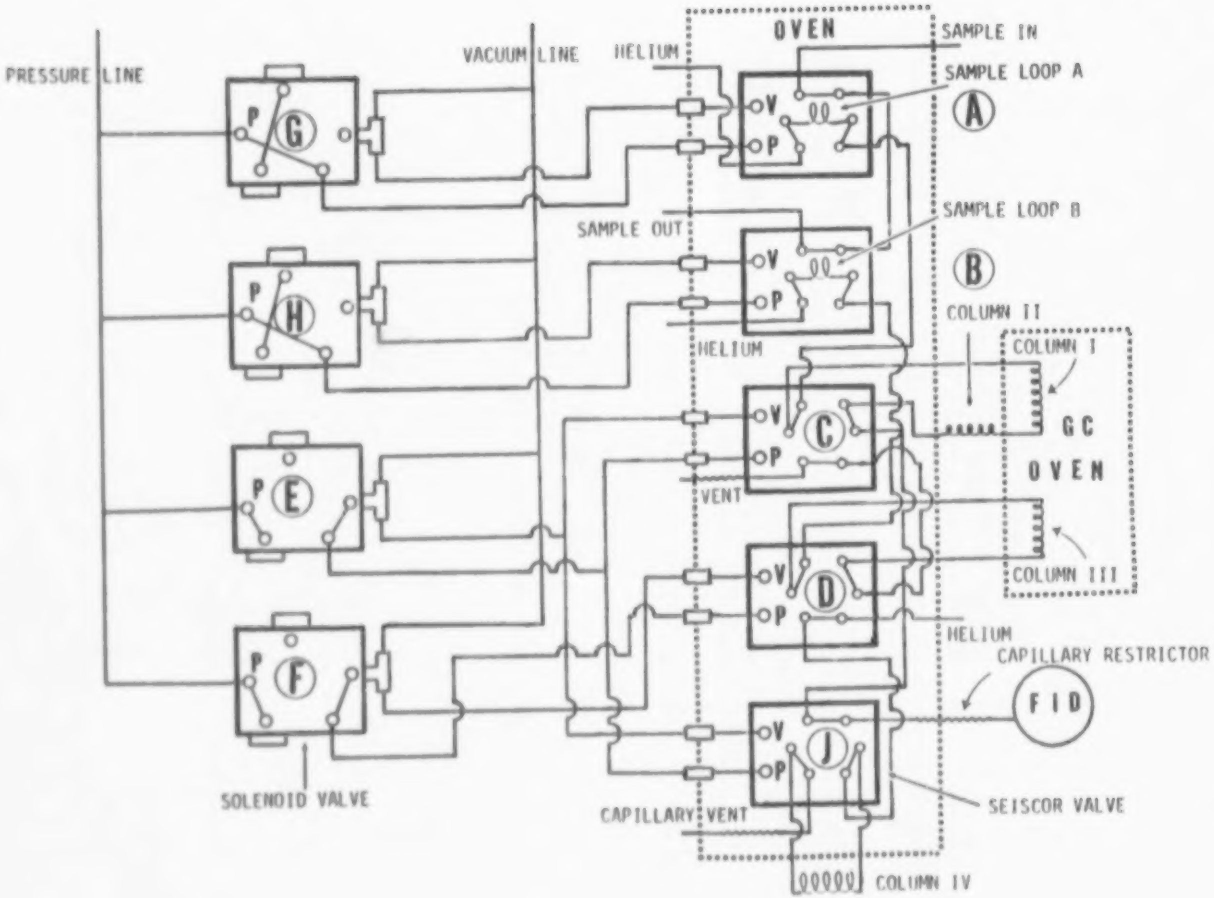

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
G
V
P
SAMPLE OUT
SAMPLE LOOP B
B
H
HELIUM
COLUMN II
COLUMN I
GC
OVEN
C
E
VENT
COLUMN III
D
HELIUM
CAPILLARY RESTRICTOR
FID
F
J
SOLENOID VALVE
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV

Figure 5. Step 2 solenoid H activation of gas sampling valve B.

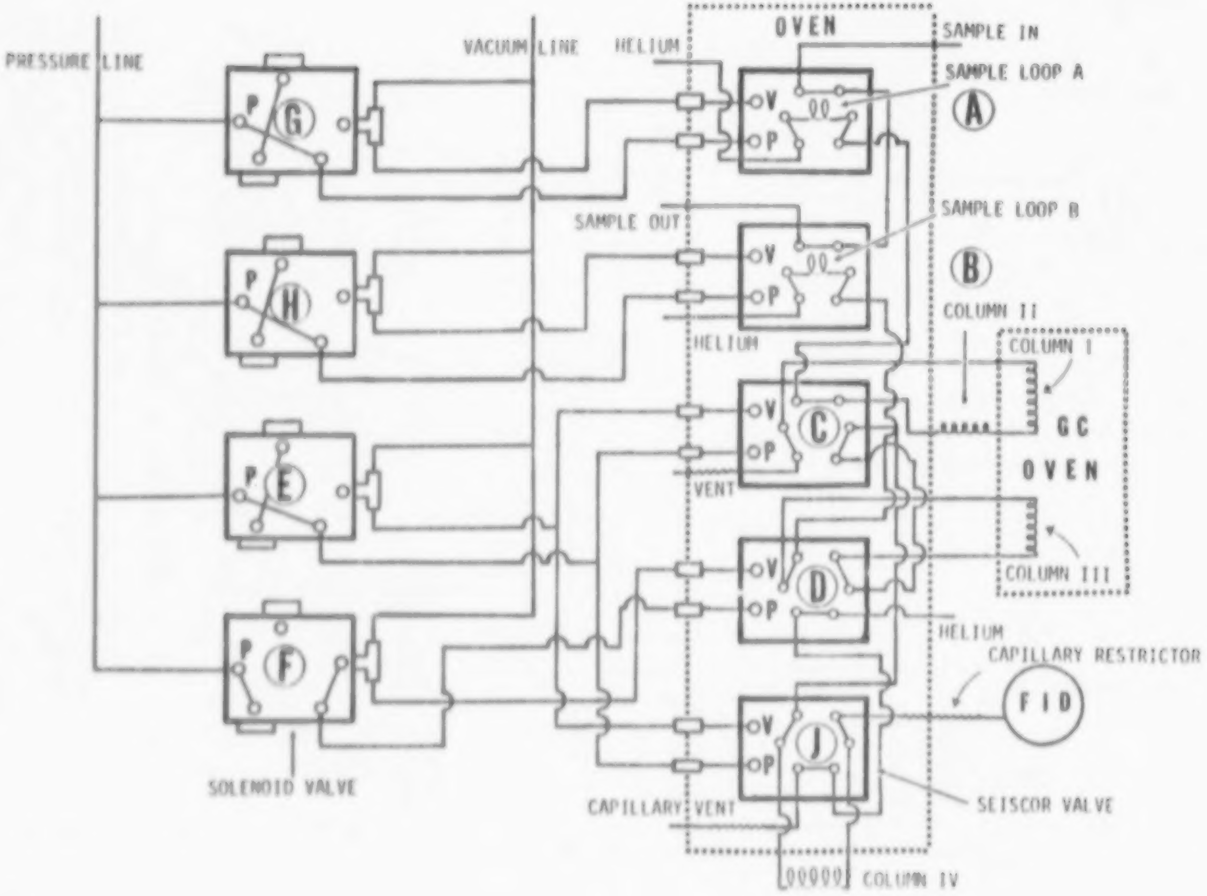

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
G
H
E
F
V
P
SAMPLE OUT
SAMPLE LOOP B
B
HELIUM
COLUMN II
COLUMN I
GC
OVEN
C
VENT
D
COLUMN III
HELIUM
CAPILLARY RESTRICTOR
FID
J
SOLENOID VALVE
CAPILLARY
VENT
SEISCOR VALVE
COLUMN IV

Figure 6. Step 3 solenoid E activation of gas sampling valves C and J.

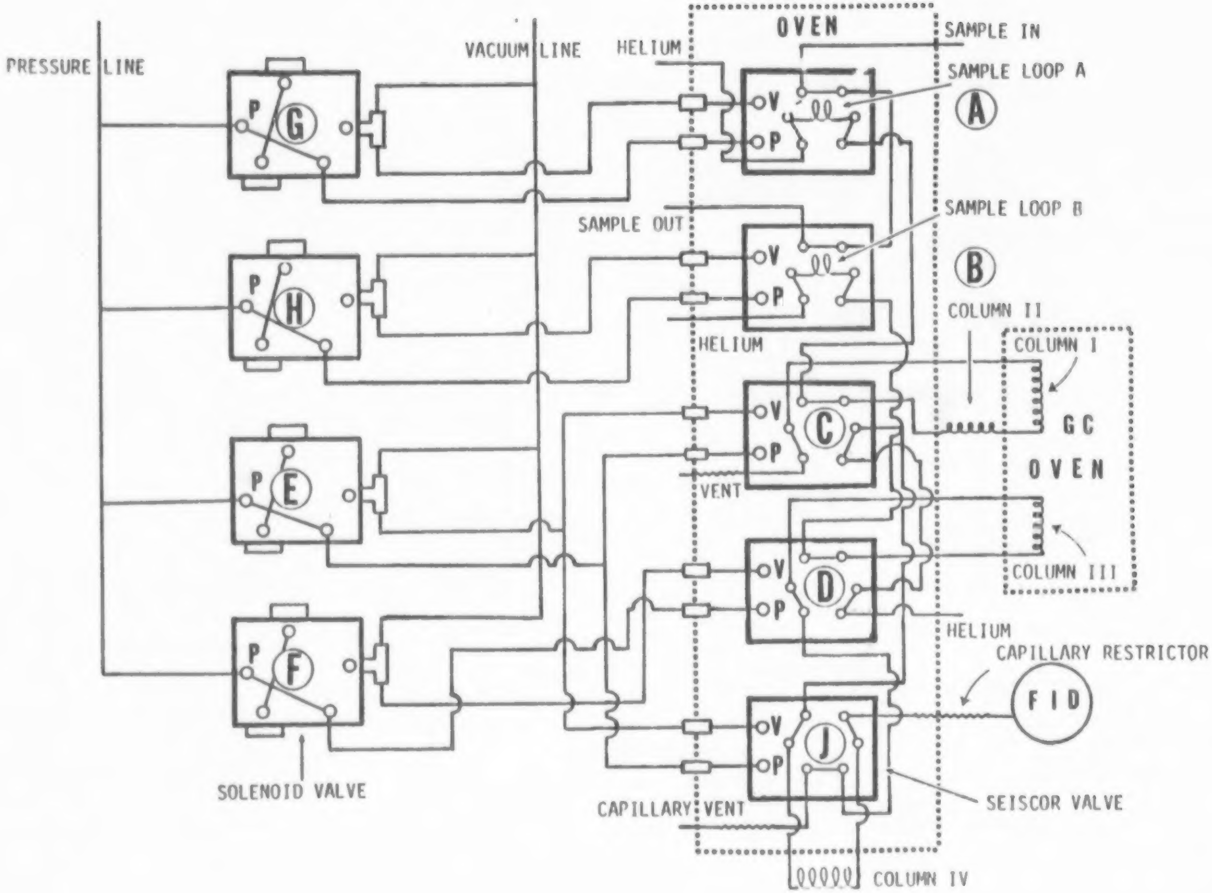

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
SAMPLE OUT
SAMPLE LOOP B
B
HELIUM
COLUMN II
COLUMN I
GC
OVEN
COLUMN III
VENT
HELIUM
CAPILLARY RESTRICTOR
FID
G
H
E
F
C
D
J
P
V
SOLENOID VALVE
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV

Figure 7. Final analytical system configuration.

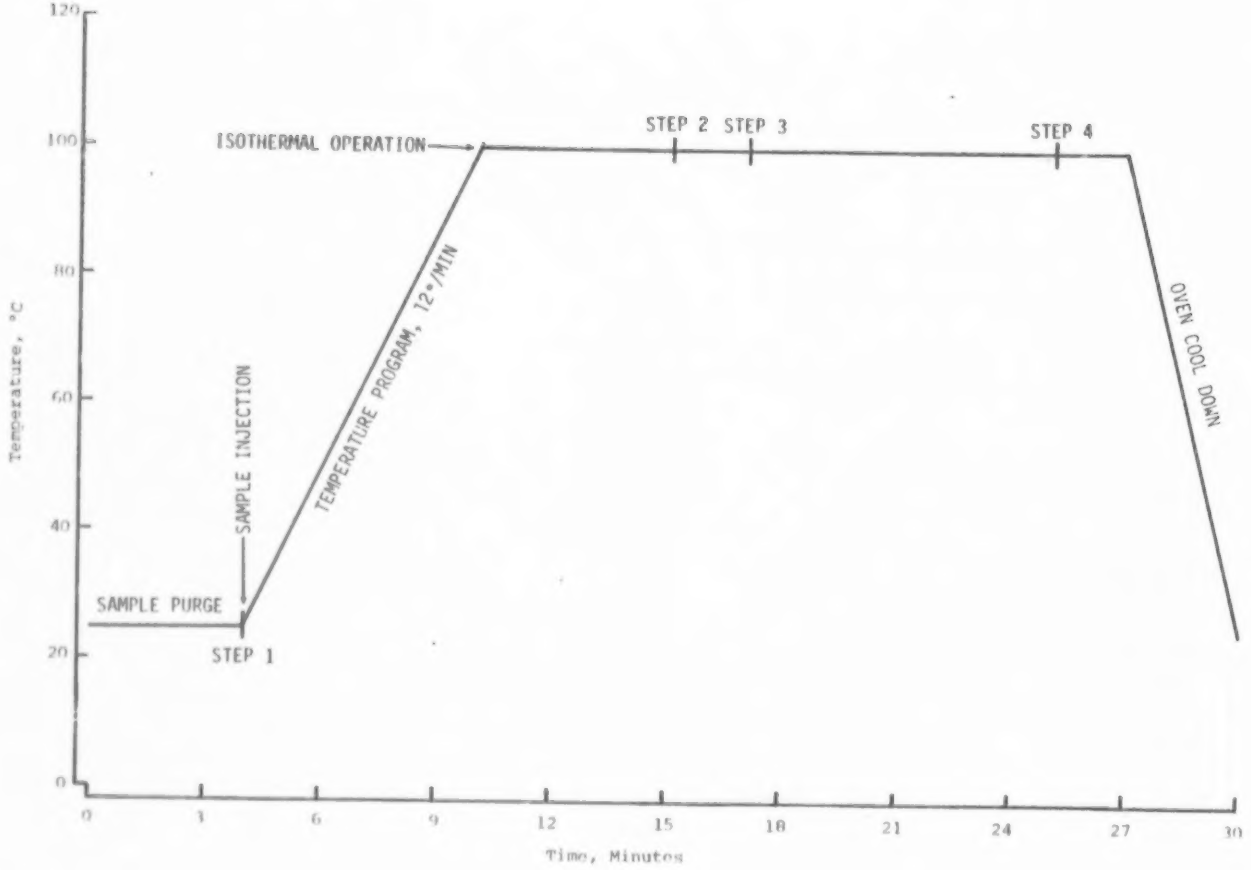


Figure 8. System operation sequence.

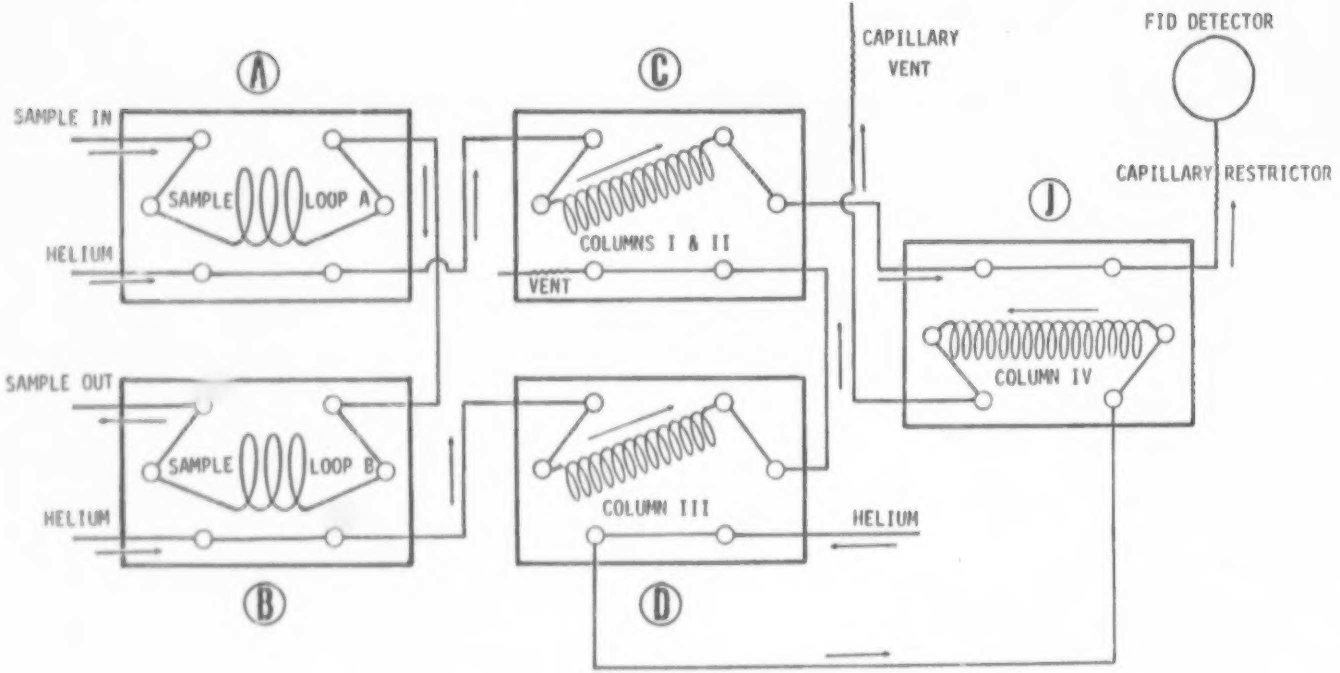

A
C
CAPILLARY VENT
FID DETECTOR
CAPILLARY RESTRICTOR
J
SAMPLE IN
SAMPLE
LOOP A
HELIUM
COLUMNS I & II
VENT
COLUMN IV
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
COLUMN III
HELIUM
B
D

Figure 9. Sample purge position prior to sample injection.

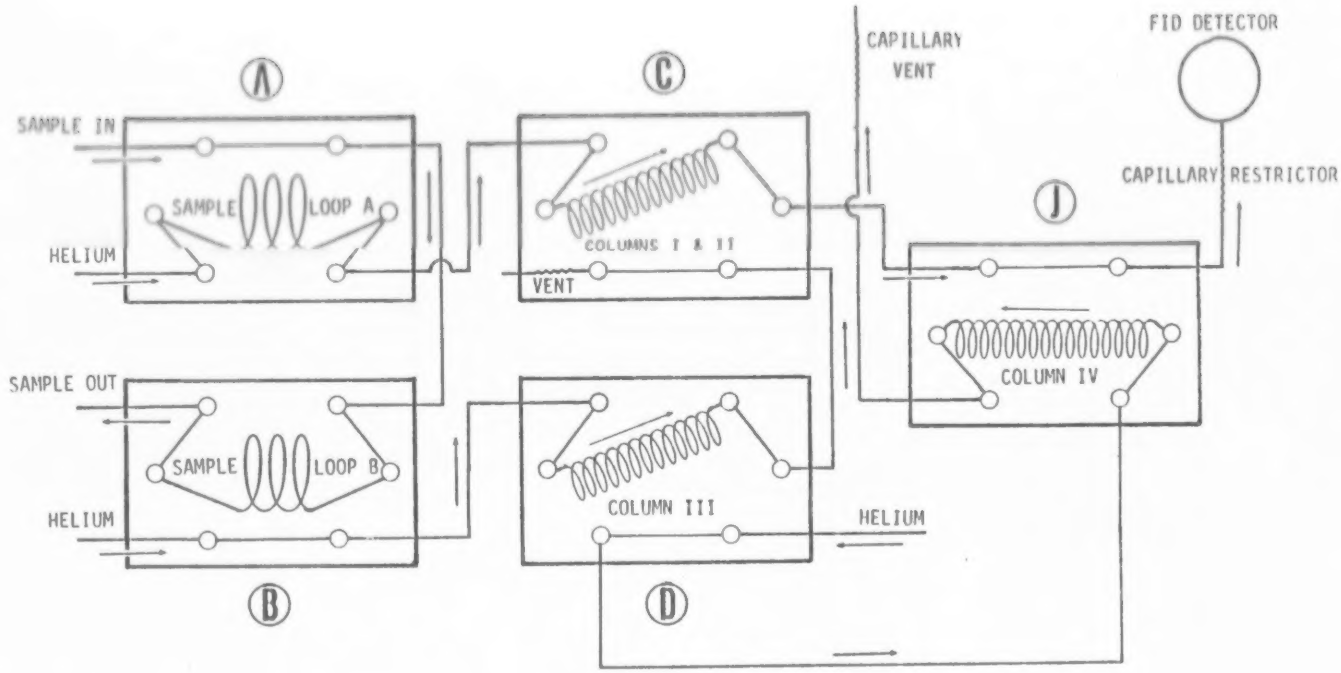

A
SAMPLE IN
SAMPLE
LOOP A
HELIUM
C
COLUMNS I & II
VENT
CAPILLARY
VENT
FID DETECTOR
CAPILLARY RESTRICTOR
J
COLUMN IV
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
B
COLUMN III
HELIUM
D

Figure 10. Step 1 sample loop A injected.

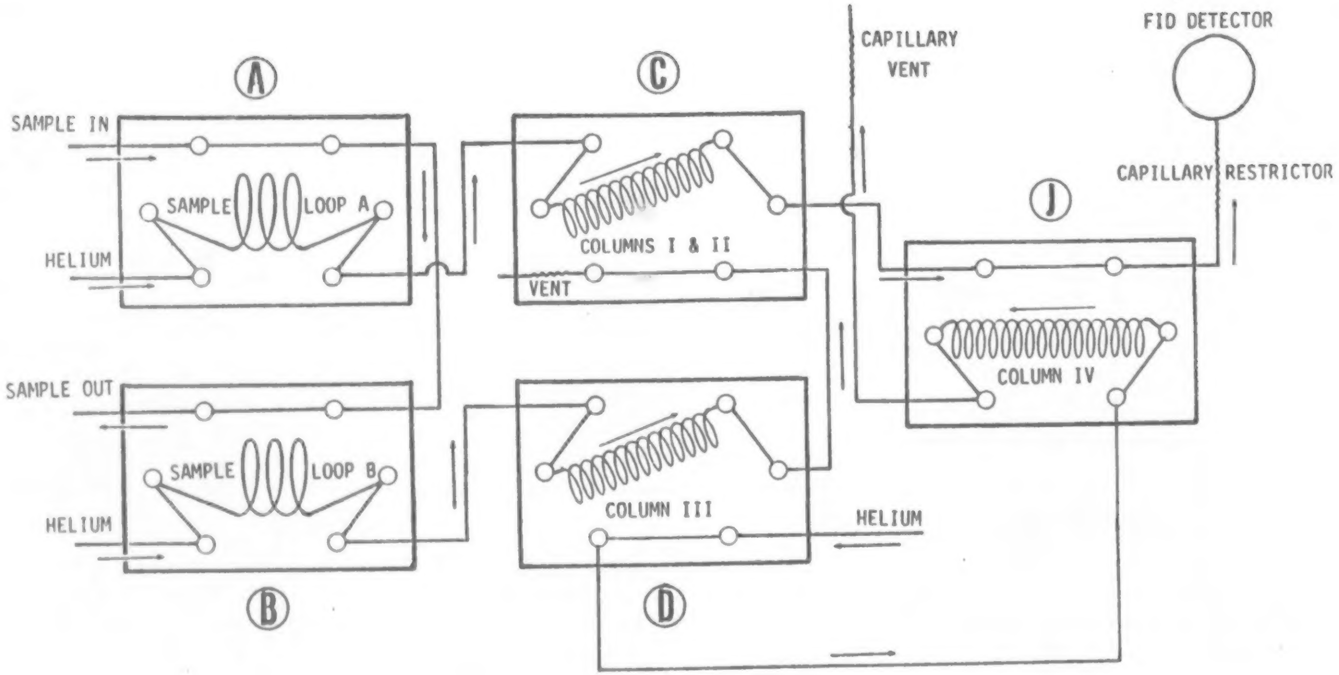

SAMPLE IN
HELIUM
SAMPLE OUT
HELIUM
A
SAMPLE
LOOP A
B
SAMPLE
LOOP B
C
COLUMNS I & II
VENT
D
COLUMN III
HELIUM
CAPILLARY
VENT
J
COLUMN IV
FID DETECTOR
CAPILLARY RESTRICTOR

Figure 11. Step 2 sample loop B injected.

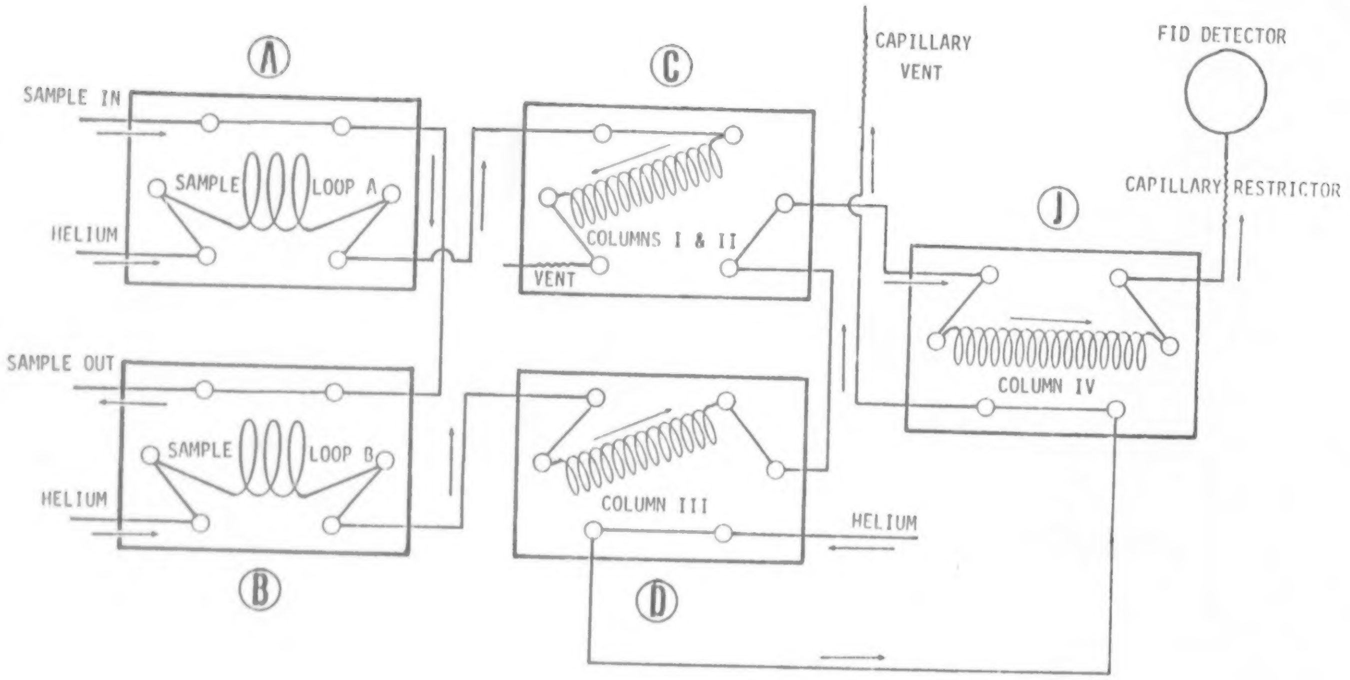

Ⓐ
SAMPLE IN
SAMPLE
LOOP A
HELIUM
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
Ⓑ
Ⓒ
COLUMNS I & II
VENT
COLUMN III
HELIUM
Ⓓ
CAPILLARY
VENT
FID DETECTOR
CAPILLARY
RESTRICTOR
Ⓙ
COLUMN IV

Figure 12. Step 3 simultaneous solenoid C and J activation.

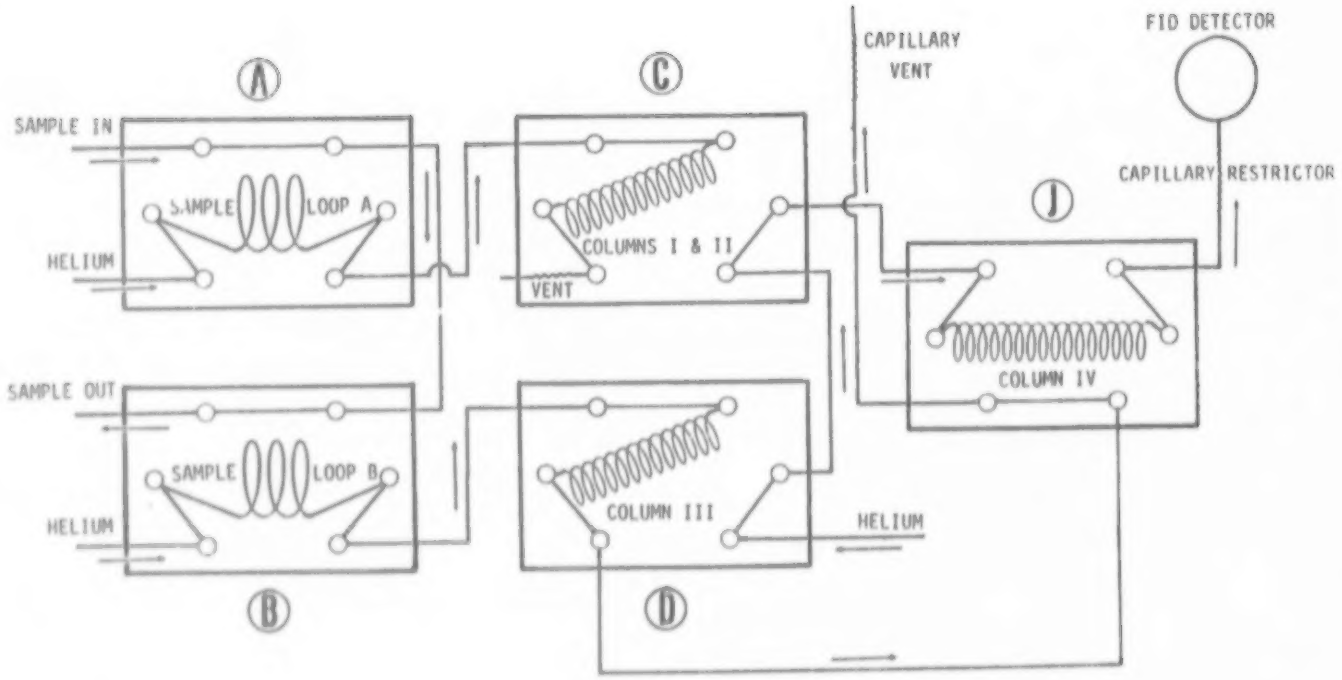

A
C
CAPILLARY
VENT
FID DETECTOR
SAMPLE IN
SAMPLE
LOOP A
HELIUM
COLUMNS I & II
VENT
CAPILLARY RESTRICTOR
J
COLUMN IV
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
COLUMN III
HELIUM
B
D

Figure 13. Step 4 backflushing of column III.

trapped sample in sample loop B routed to Column III. Figure 11 demonstrates Step 2. Gas sampling valves C and J are simultaneously switched to backflush Columns I and II and direct the sample in sample loop B through Column III and Column IV and then to the detector in Step 3. Finally, Step 4 results in the backflushing of Column III to the vent. The system remains in this configuration until it is reset to the initial purge position. A sample chromatogram for the calibration blend of individual hydrocarbons is shown in Figure 14.

CONTROL SYSTEM

The control of the five Seiscor gas sampling valves is accomplished by ATC timers and ASCO electric solenoid valves. With the solenoid valve in the de-energized configuration, the gas sampling valve is in one position. An electrical impulse from the timer energizes the solenoid valve. The pressure difference created in the gas sampling valve changes the position. Figure 15 illustrates the de-energized and energized configuration for solenoid valve G and gas sampling valve A. This accomplishes the complicated column flow sequence required for this analysis. The system repeatability is ± 1.8 percent.

CALCULATIONS

The concentration of the individual hydrocarbons are compared to a calibration blend with known concentrations of each of the components. The peak areas are determined with a Hewlett-Packard Model 3354 computer system and printed out on a remote teletype unit. The concentration of the sample is determined with the equation:

$$\frac{Astd_n}{Cstd_n} = \frac{Asam_n}{Csam_n}$$

where Astd = the peak area of component n in the calibration blend
Cstd = the concentration of component n in the calibration blend
Asam = the peak area of component n in the sample
Csam = the unknown concentration of component n in the sample
n = the component of interest (i.e., methane, ethylene, ethane, acetylene, propane, propylene, benzene, or toluene)

If the equation is solved of Csam, the result is:

$$Csam_n = \frac{Asam_n \times Cstd_n}{Astd_n}$$

Example 1:

A bag sample was taken from the exhaust stream of a vehicle during a driving cycle. The peak area of the calibration blend for methane was 11893 area counts with a concentration of 13.616 ppmC. The peak area of methane in the sample was 8593 area counts. Calculate the concentration of methane in the exhaust.

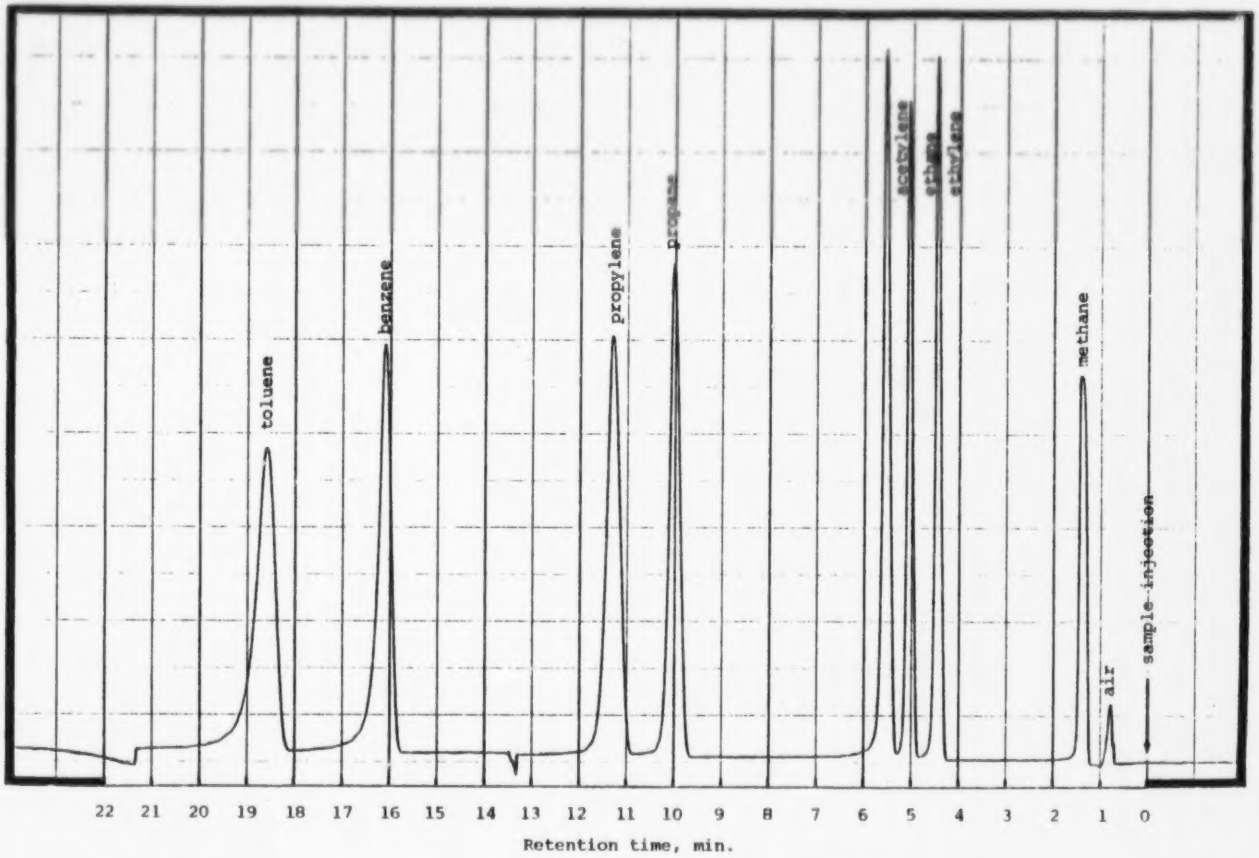
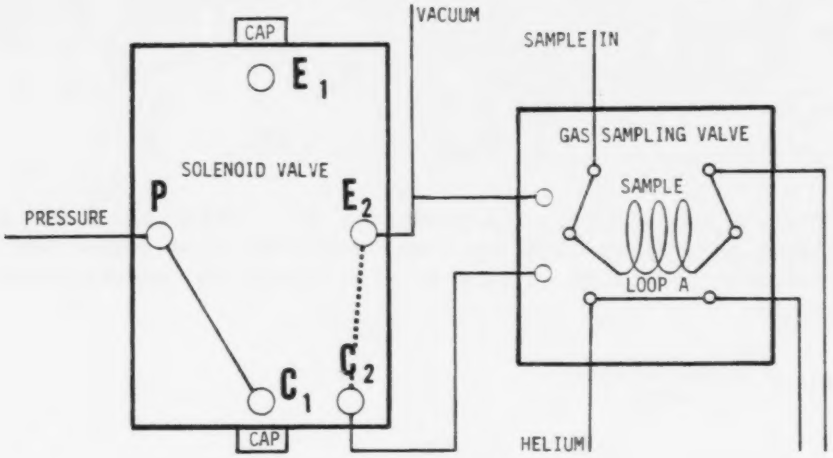
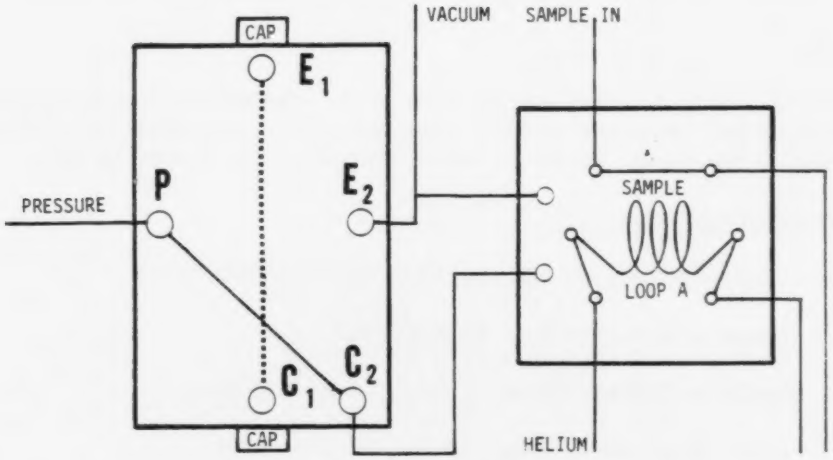


Figure 14. Calibration blend for specific hydrocarbons.


VACUUM
SAMPLE IN
CAP
E1
GAS SAMPLING VALVE
SOLENOID VALVE
SAMPLE
P
E2
PRESSURE
LOOP A
C2
C1
CAP
HELIUM

de-energized configuration


VACUUM
SAMPLE IN
CAP
E1
SAMPLE
P
E2
PRESSURE
LOOP A
C2
C1
CAP
HELIUM

energized configuration

Figure 15. Solenoid valve G with gas sampling valve A

$$\mathrm{Csam}_n = \frac{\mathrm{Asam}_n \times \mathrm{Cstd}_n}{\mathrm{Astd}_n}$$

$$\mathrm{Csam\ (methane)} = \frac{(8593)\ (13.616)}{(11893)}$$

Csam (methane) = 9.84 ppm C

Example 2:

In the sample analysis, the peak area for toluene was 10973 area counts. The peak area for the calibration blend was 18546 area counts for toluene with a concentration of 21.272 ppm C. Calculate the concentration of toluene in the sample.

$$\mathrm{Csam}_n = \frac{\mathrm{Asam}_n \times \mathrm{Cstd}_n}{\mathrm{Astd}_n}$$

$$\mathrm{Csam\ (toluene)} = \frac{(10973)\ (21.272)}{(18546)}$$

Csam (toluene) = 12.59 ppm C

Note: These sample calculations are presented as a example only and are not necessarily representative of expected values in exhaust.

EQUIPMENT

This analysis is performed using a gas chromatograph equipped with a flame ionization detector (FID). The equipment required is divided into two categories. The major items in each category are listed below:

Gas Chromatograph Detection

1. Varian Aerograph Series 1400 Gas Chromatograph
2. Leeds and Northrup 1 mv Recorder
3. Hewlett-Packard Model 3354 Computer System
4. Hewlett-Packard Model 1865A A/D Converter

Control Console System

1. Seiscor Model VIII Gas Sampling Valve
2. ATC Timers, Model 325A346A10PX
3. ASCO 4-way Midget Solenoid Valve, No. 8345B

4. Thomas Sample Pump, Model 106 CA18
5. Brooks Flowmeter, R-2-15-AAA with glass float, 0-15 Scale
6. Miscellaneous stainless steel and brass nuts, ferrules, unions, tees, connectors, etc.
7. Miscellaneous stainless steel, copper, and Telfon tubing
8. Bendix Valve Oven
9. Column I, 8' x 1/8" SS, 80/100 mesh Porapak Q
10. Column II, 4' x 1/8" Teflon, 36/60 mesh Type 58 Silica Gel
11. Column III, 15' x 1/8" SS, 15 percent 1, 2, 3-tris (cyanoethoxy) Propane on 60/80 mesh Chromosorb PAW
12. Column IV, 2' x 1/8" SS, 40 percent $HgSO_4$ on Chromosorb W
13. Miscellaneous electrical switches, wiring, lights, etc.

REFERENCES

Altshuller, A.P. and Bufalini, J.J. Environ. Sci. Tech., Vol. 5, pg. 39, 1971.

Federal Register, Vol. 37, No. 221, 24270-77 Nov. 1971.

Klosterman, D.L. and Sigsby, J.E., Environ. Sci. Tech., Vol. 1, pg 309, 1967.

Rasmussen, R.A. and Holdren, M.W., Chromatog. Newslett., Vol. 1, No. 2, pg. 31, 1972.

Dimitriades, B. and Seizenger, E.D., Environ. Sci. Tech., Vol. 5, No. 3, pg. 223, 1979.

Purcell, J.E. and Gilson, C.P., Chromatog. Newslett., Vol. 1, No. 2, pg 45, 1972.

Stuckey, C.L., J. Chromatog. Sci., Vol. 7, pg. 177, 1969.

Papa, L.J., Dinsel, D.L., and Harris, W. C., J. Gas Chromatog., Vol. 6, pg. 270, 1968.

Black, F.M., High, L.E. and Sigsby, J.E., J. Chromatog. Sci., Vol. 14, pg. 257, May 1976.

Private communication between Mobile Source Emissions Research Branch, ESRL-EPA, Research Triangle Park and Southwest Research Institute.

APPENDIX D

ORGANIC AMINES PROCEDURE

THE MEASUREMENT OF ORGANIC AMINES IN EXHAUST

The organic amines that are included in this analysis are: monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, and triethylamine. Dimethylamine and monoethylamine are not resolved from each other under normal operating conditions and are reported together as C_2H_7N. The measurement of organic amines in exhaust is accomplished by bubbling the exhaust through glass impingers containing dilute sulfuric acid. The amines are complexed by the acid to form stable sulfate salts which remain in solution. The exhaust sample is collected continuously during the test cycle. For analysis, a portion of the sulfuric acid solution is injected into a gas chromatograph equipped with an ascarite loaded pre-column and a nitrogen phosphorus detector (NPD). External amine standards in dilute sulfuric acid are used to quantify the results. Detection limits for this procedure are on the order of 0.002 ppm in dilute exhaust.

SAMPLING SYSTEM

A glass impinger containing 25 mℓ of 0.01 N sulfuric acid is used to collect exhaust samples for the analysis of the organic amines. A flow schematic of the sample collection system is shown in Figure 1. The single glass impinger is sufficient to collect 99+ percent of the organic amines. The temperature of the impinger is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4ℓ/minute by the sample pump. A dry gas meter is used to determine the total flow through the impinger during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allows continuous monitoring of the sample flow to insure proper flow rates during the sampling. When sampling from diesel fueled vehicles, a heated filter, located between the solenoid valve and the dilution tunnel, is used to prevent diesel particulate from contaminating the sampling system. The filter and the line connecting the filter to the dilution tunnel are heated to 375°F in order to keep the organic amines from being retained on the removed particulate. The Teflon line connecting the heated filter and the solenoid valve is heated to ~175°F in order to prevent water from condensing in the sample line. Several views of the sampling system are shown in Figure 2.

ANALYTICAL PROCEDURE

The analysis of the organic amines (monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, and triethylamine) is

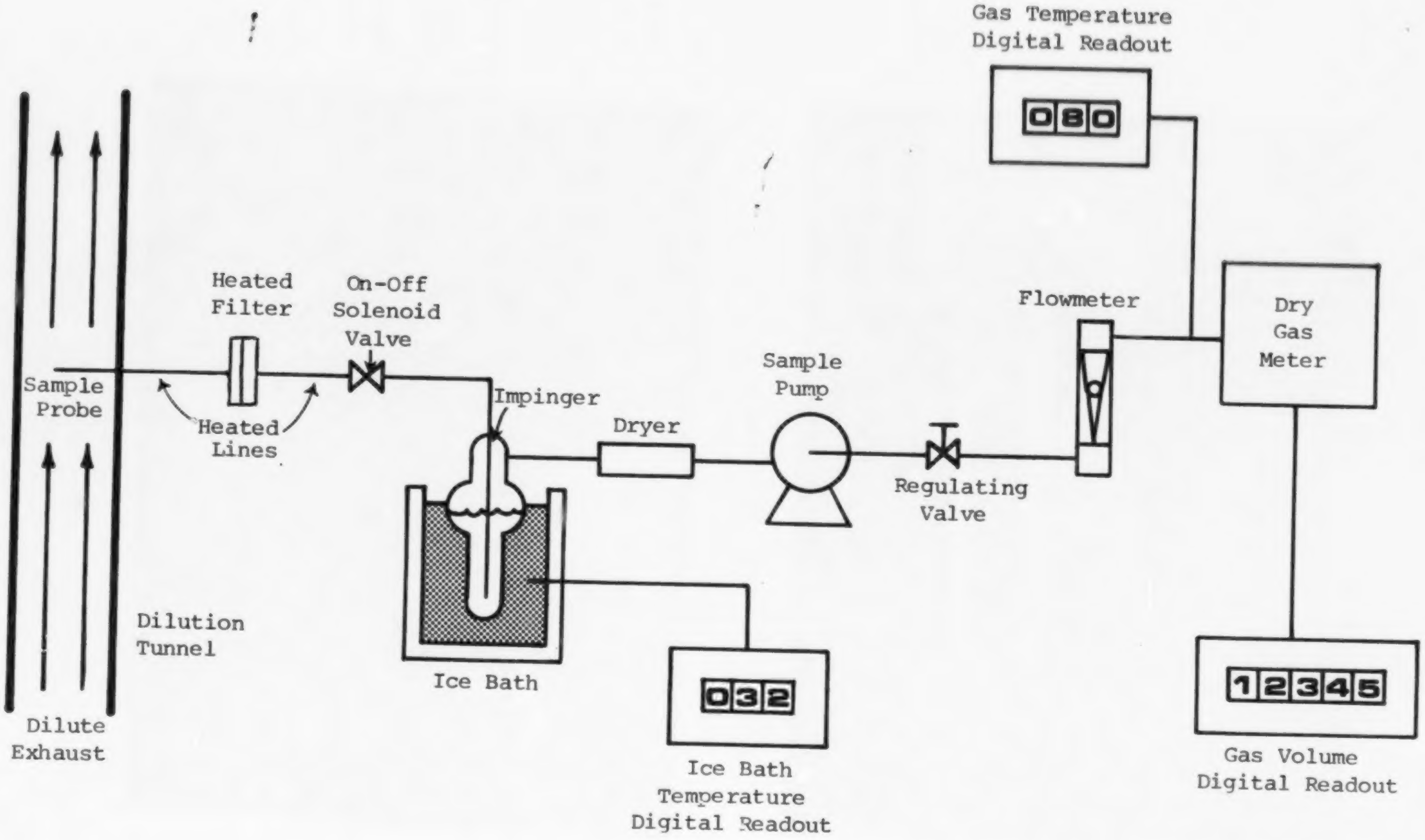
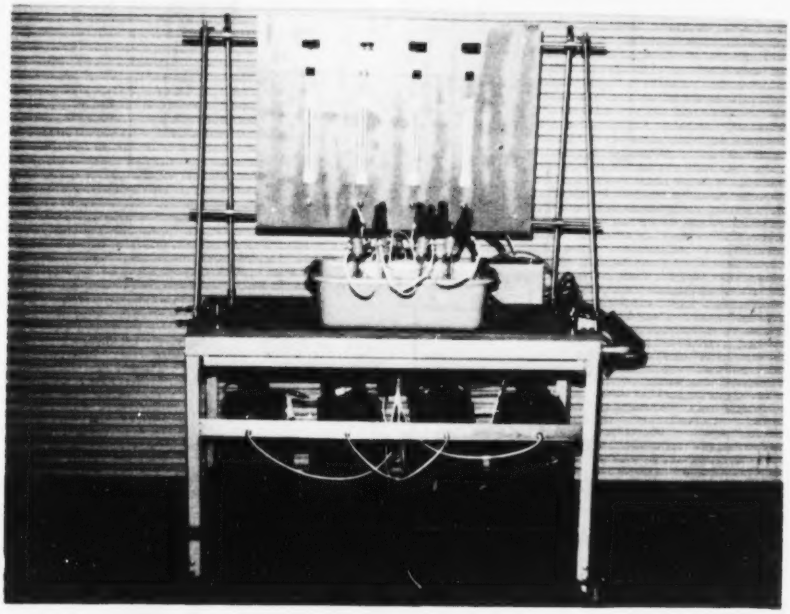
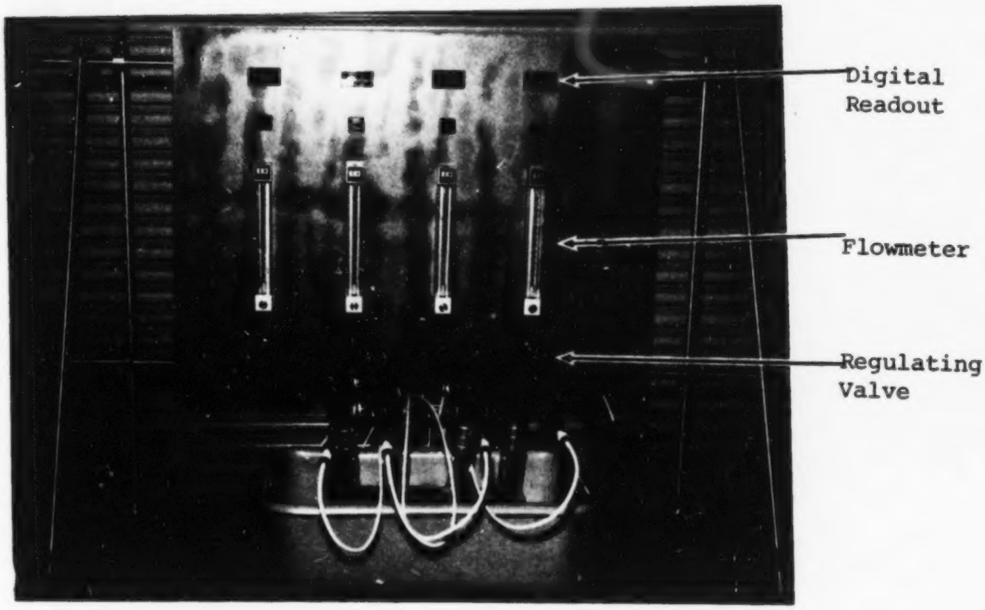

Gas Temperature
Digital Readout
080
Heated
Filter
On-Off
Solenoid
Valve
Flowmeter
Dry
Gas
Meter
Sample
Pump
Sample
Probe
Impinger
Dryer
Heated
Lines
Regulating
Valve
Dilution
Tunnel
Ice Bath
032
12345
Dilute
Exhaust
Ice Bath
Temperature
Digital Readout
Gas Volume
Digital Readout

Figure 1. Organic amines sample collection flow schematic.



Front View


Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

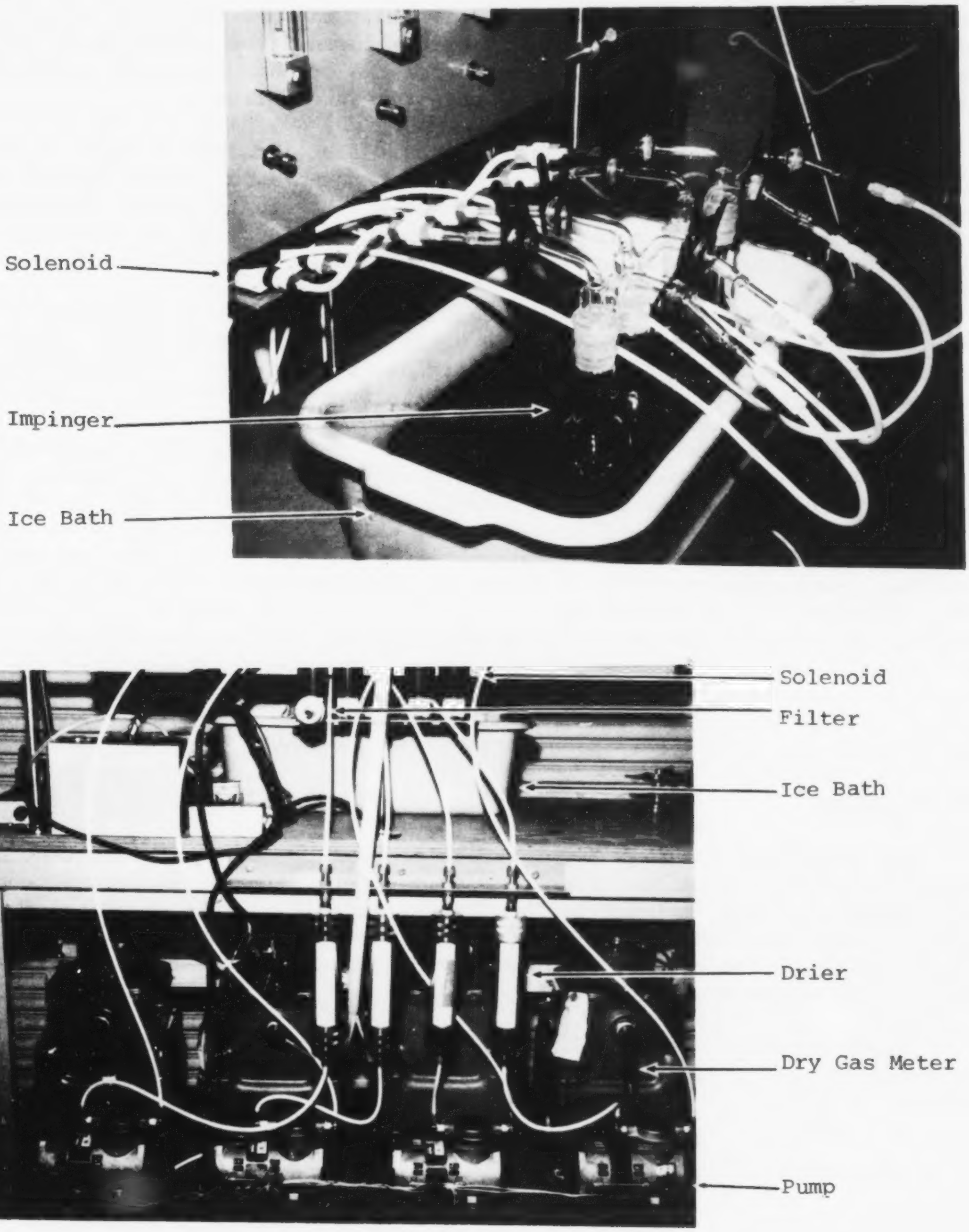

Solenoid
Impinger
Ice Bath
Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Figure 2 (Cont'd). Organic amines sampling system.

accomplished by trapping the amines in sulfuric acid and analyzing the sample with a gas chromatograph equipped with an NPD. The NPD is highly sensitive to organic nitrogen compounds and relatively insensitive to inorganic nitrogen compounds. The analysis flow schematic for the organic amines is shown in Figure 3. A detailed description of the procedure follows.

For the analysis of the organic amines, dilute exhaust is bubbled through a glass impinger containing 25 mℓ of 0.01 N sulfuric acid. Upon completion of each driving cycle, the impinger is removed and the contents are transferred to a 30 mℓ polypropylene bottle and capped. The amines, as their sulfate salts, can be stored in solution for long periods of time without decomposition.

A Perkin-Elmer 3902B gas chromatograph equipped with an ascarite loaded pre-column, a Teflon interface, and a nitrogen phosphorus detector (NPD) is used to analyze the sample. A 10 μℓ portion of the sample is injected into the gas chromatograph (GC). In the ascarite pre-column, Figure 4, the amines are released from their sulfate salts into the GC column. The column is a 6" x 4 mm glass column containing Carbopack B coated with 4 percent Carbowax 20 M and 0.8 percent KOH. The column effectively separates the amines, with the exception of ethylamine and dimethylamine, which are reported together as total C_2H_7N. The carrier gas is helium which flows through the column at a rate of 30 mℓ/minute. The column temperature is 130°C for 4 minutes and then programmed to 170°C at a rate of 32° a minute. In a chromatogram of a standard sample containing all six of the amines, Figure 5, the first peak is monomethylamine, followed by the combined peak of dimethylamine and monoethylamine, C_2H_7N, and then by peaks of trimethylamine, diethylamine, and triethylamine. To quantify the results, the sample peak areas are compared to peak areas of standard solutions. Figure 6 shows the analytical system with gas chromatograph, detector, A/D converter, and recorder.

CALCULATIONS

The procedure has been developed to provide the user with the concentration of the organic amines (monomethylamine, total dimethylamine and monoethylamine as C_2H_7N, trimethylamine, diethylamine, and triethylamine) in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm for each of the amines. The equations for determining the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92"Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

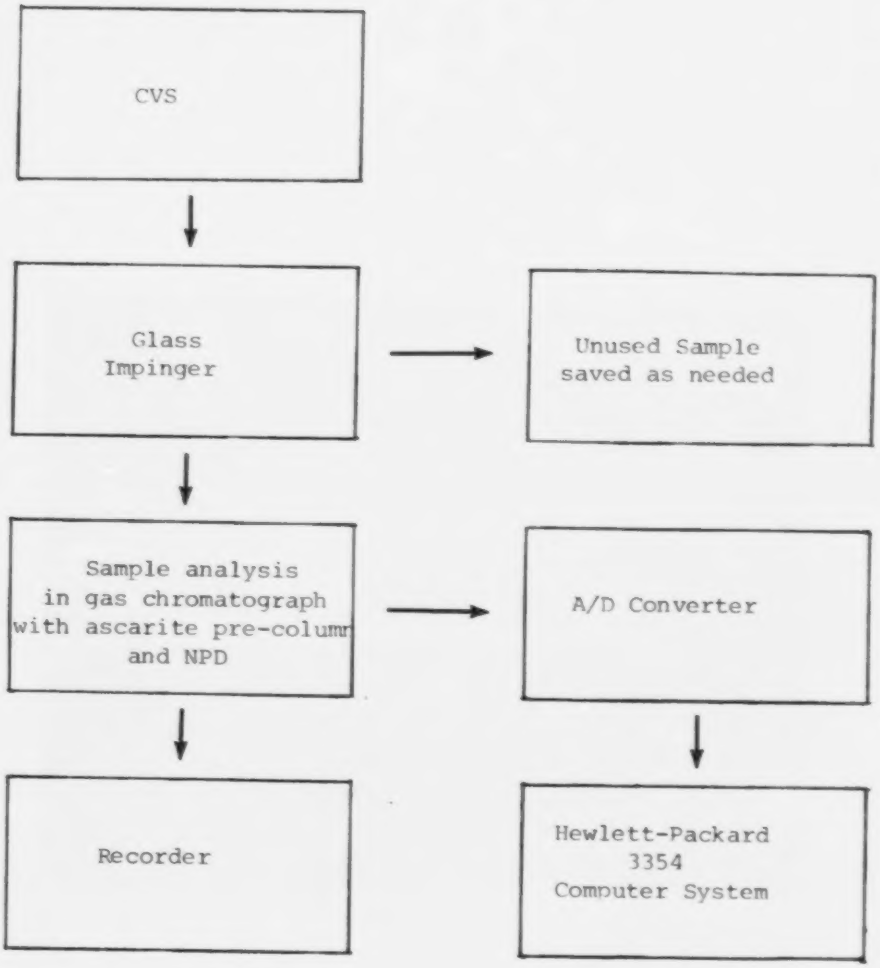

CVS
Glass Impinger
Unused Sample saved as needed
Sample analysis in gas chromatograph with ascarite pre-column and NPD
A/D Converter
Recorder
Hewlett-Packard 3354 Computer System

Figure 3. Organic amines analysis flow schematic.

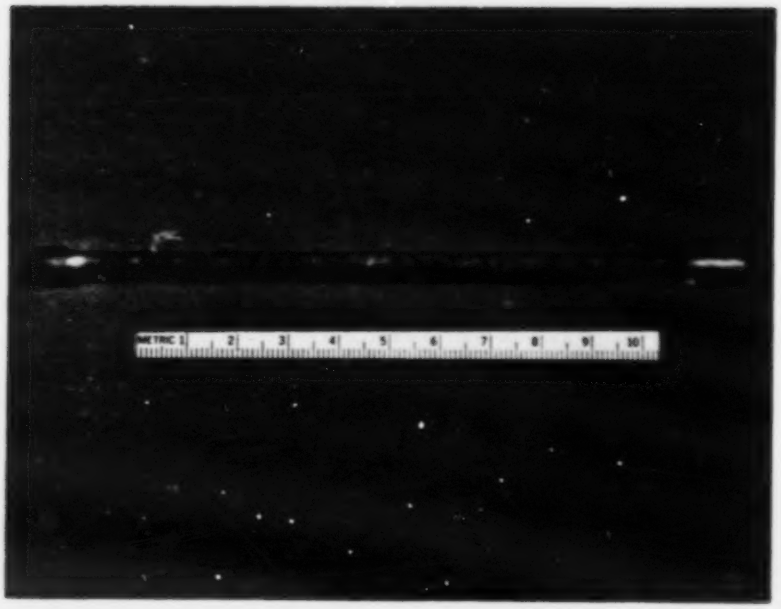
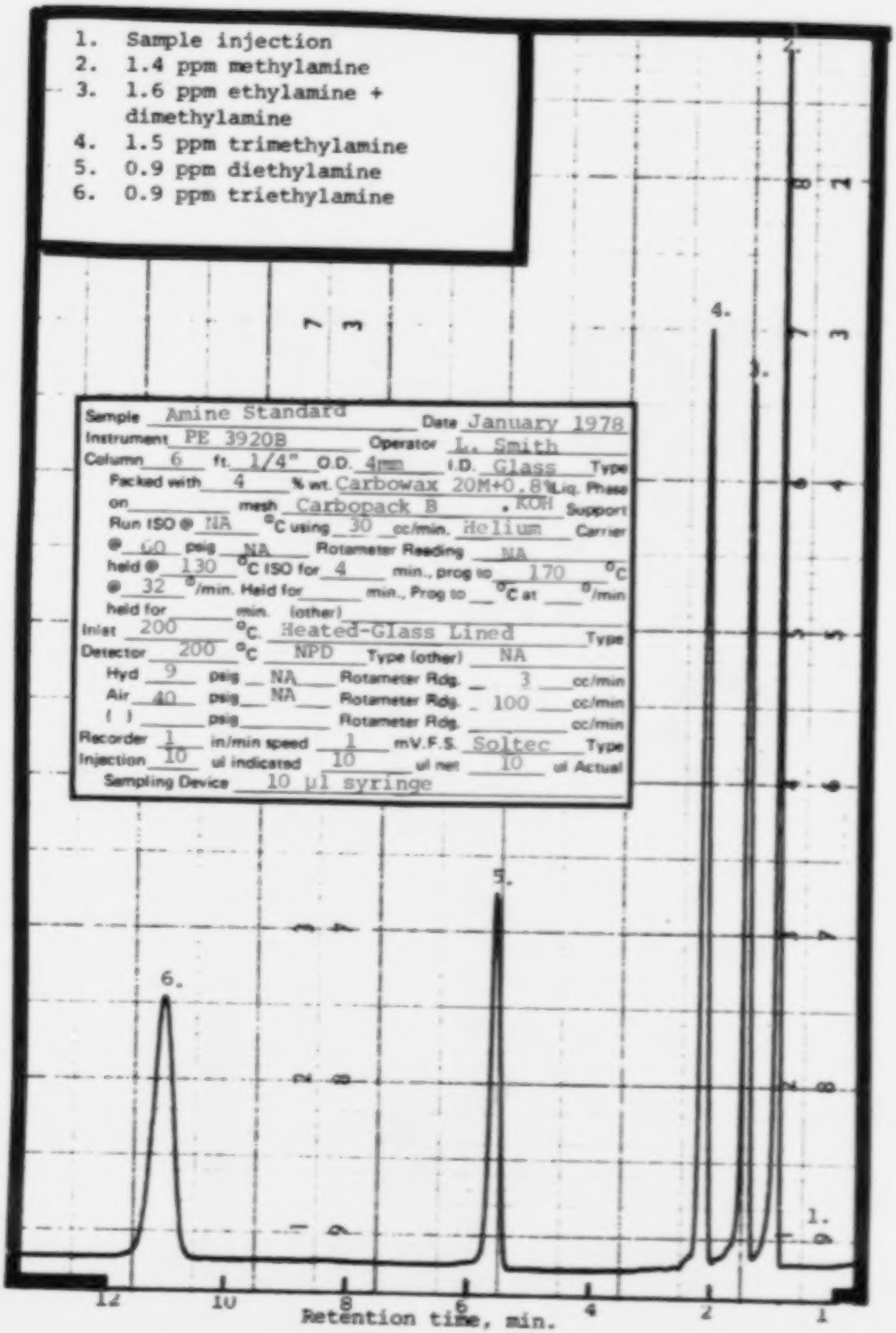

METRIC 1 2 3 4 5 6 7 8 9 10

Figure 4. Ascarite pre-column.



1. Sample injection
2. 1.4 ppm methylamine
3. 1.6 ppm ethylamine + dimethylamine
4. 1.5 ppm trimethylamine
5. 0.9 ppm diethylamine
6. 0.9 ppm triethylamine

Sample Amine Standard Date January 1978
Instrument PE 3920B Operator L. Smith
Column 6 ft. 1/4" O.D. 4mm I.D. Glass Type
Packed with 4 % wt. Carbowax 20M+0.8% KOH Liq. Phase
on ____ mesh Carbopack B Support
Run ISO @ NA °C using 30 cc/min. Helium Carrier
@ 60 psig NA Rotameter Reading NA
held @ 130 °C ISO for 4 min., prog to 170 °C
@ 32 °/min. Held for ____ min., Prog to ____ °C at ____ °/min
held for ____ min. (other) ____
Inlet 200 °C. Heated-Glass Lined Type
Detector 200 °C NPD Type (other) NA
Hyd 9 psig NA Rotameter Rdg. 3 cc/min
Air 40 psig NA Rotameter Rdg. 100 cc/min
( ) ____ psig ____ Rotameter Rdg. ____ cc/min
Recorder 1 in/min speed 1 mV.F.S. Soltec Type
Injection 10 ul indicated 10 ul net 10 ul Actual
Sampling Device 10 µl syringe

Figure 5. Chromatogram of amine standard.

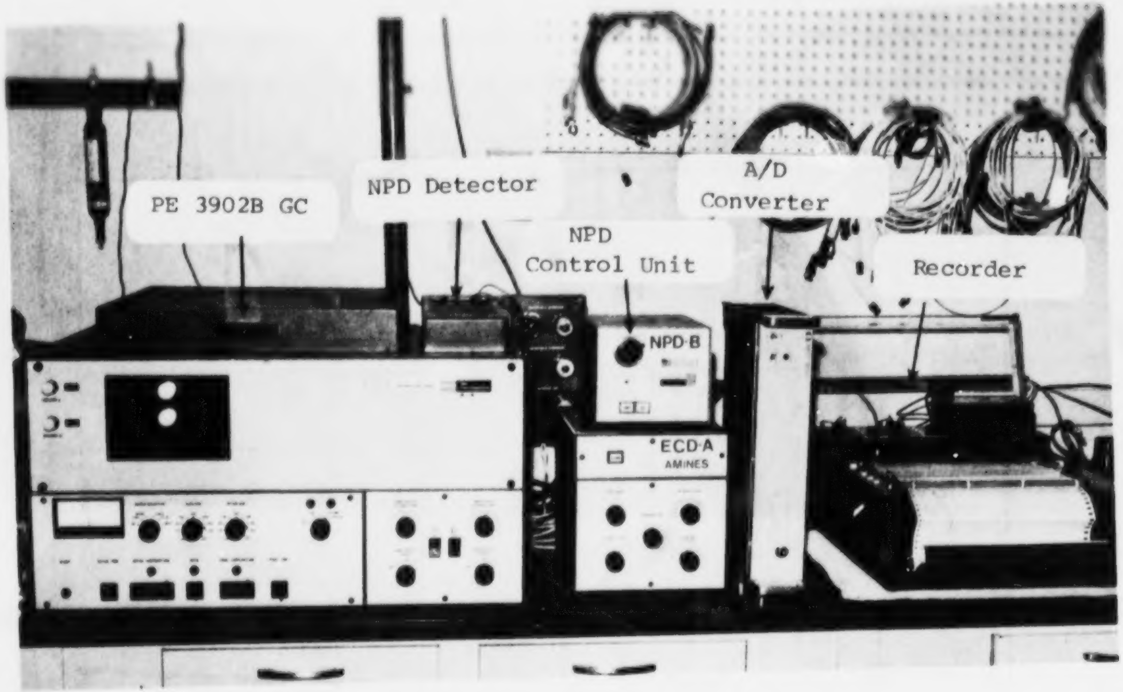

PE 3902B GC
NPD Detector
NPD
Control Unit
A/D
Converter
Recorder
NPD-B
ECD-A
AMINES

Figure 6. Total amine analytical system.

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92"Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92"Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{"Hg}}$$

The next step converts the volume from cubic feet to cubic meters by use of the conversion factor; 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr(m^3)} = \frac{P_{exp}(\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°}{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)

The next step is to find the concentration of each of the amines in μg/mℓ. Since the gas chromatograph NPD has a linear response in the concentration of concern, then the following equation holds.

$$\frac{C_{sam}\ (\mu g/m\ell)}{A_{sam}} = \frac{C_{std}\ (\mu g/m\ell)}{A_{std}}$$

C_{sam} = concentration of the sample is μg/mℓ
A_{sam} = GC peak area of sample in relative units
C_{std} = concentration of the standard in μg/mℓ
A_{std} = GC peak area of standard in relative units

Solving for C_{sam} gives:

$$C_{sam}(\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam}}{A_{std}}$$

The $C_{sam}(\mu g/m\ell)$ in solution is corrected for any necessary dilution by multiplying by the dilution factor, D.F.

$$C_{sam}(\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F.}{A_{std}}$$

To obtain the total amount in μg of each amine in the absorbing solution, the absorbing reagent volume is multiplied by the concentration to give:

$$\mu g \text{ sample} = C_{sam}\ (\mu g/m\ell) \times \text{Abs. Vol. } (m\ell)$$

$$= \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{A_{std}}$$

(Equation 2)

To obtain μg sample/m^3, Equation 2 is divided by Equation 1 to give:

$$\mu g \text{ samp}/m^3 = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg}) \times 528°}$$

$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ (ft^3/m^3)}{V_{exp}\ (ft^3)}$$

(Equation 3)

To find the concentration of each amine in ppm, the densities of the amines are needed. At 29.92"Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation

$$\frac{V}{T} = \frac{V_1}{T_1}$$

$V_1 = 22.4\ell$
$T_1 = 32°F + 460 = 492°R$
V = volume at 68°F
$T = 68°F + 460 = 528°R$

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04ℓ at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 22.04 ℓ/mole

$$\text{den } (g/\ell) = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}}$$

The density in μg/mℓ can be found by converting g to μg and ℓ to mℓ as follows:

$$\text{den } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04 \ \ \ell/\text{mole}} \times \frac{1 \times 10^6 \mu g/g}{1 \times 10^3 m\ell/\ell} = \frac{\text{mol. wt.} \times 1000}{24.04}$$

(Equation 4)

To obtain the concentration of each amine in ppm, the concentration in $\mu g/m^3$ is divided by the density in μg/mℓ

$$\text{ppm} = \mu g/m^3 \div \mu g/m\ell = \frac{m\ell}{m^3}$$

Using Equations 3 and 4 gives the ppm concentration in the form of the raw data.

$$\text{ppm} = \frac{24.04(\ell) \times C_{std} \ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{\text{Mol. Wt. (g/mole)} \times 1000 \times A_{std} \times P_{exp} \ (\text{"Hg})}$$

$$\times \frac{T_{exp}(°R) \times 29.92\text{"Hg} \times 35.31 \ ft^3/m^3}{528°R \times V_{exp} \ (ft^3)}$$

(Equation 5)

At this point, the concentration can be expressed in $\mu g/m^3$ (Equation 3) and ppm (Equation 5) at 68°F and 29.92"Hg from the raw data.

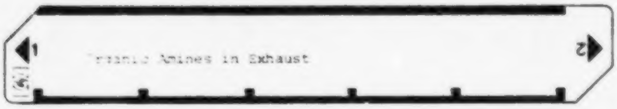
Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period, a Hewlett-Packard 67 program was developed to calculate the organic amine concentrations in $\mu g/m^3$ and ppm from the raw data. This program is presented in Figure 7.

Sample Calculation

Assume exhaust samples were collected in glass impingers for each portion of a three-bag 1975 FTP. Raw data for these tests are presented in Figure 8. Calculations were performed using the HP 67 program and manual calculations.

User Instructions



STEP	INSTRUCTIONS	INPUT DATA UNITS	KEYS	OUTPUT DATA UNITS
0_1	Switch to on: switch to run			
0_2	Feed side 1 of card in from right to left			
0_3	Set decimal place		f [illegible]	
1	Input - Sample Volume	ft^3	A	
2	Input - Barometric Pressure	"Hg	R/S	
3	Input - Sample Temperature	°F	R/S	
4	Input - Dilution Factor		R/S	
5	Input - Absorbing Reagent Vol.	mℓ	R/S	
6	Input - Standard Conc. CH_3NH_2	µg/m^3	R/S	
7	Input - Standard Area CH_3NH_2		R/S	
8	Input - Sample Area CH_3NH_2		R/S	
9	Output - Sample Conc. CH_3NH_2		R/S	µg/m^3
10	Output - Sample Conc. CH_3NH_2			ppm
11	Input - Standard Conc. C_2H_7N	µg/mℓ	R/S	
12	Input - Standard Area C_2H_7N		R/S	
13	Input - Sample Area C_2H_7N		R/S	
14	Output - Sample Conc. C_2H_7N		R/S	µg/m^3
15	Output - Sample Conc. C_2H_7N			ppm
16	Input - Standard Conc. $(CH_3)_3N$	µg/mℓ	R/S	
17	Input - Stnadard Area $(CH_3)_3N$		R/S	
18	Input - Sample Area $(CH_3)_3N$		R/S	
19	Output - Sample Conc. $(CH_3)_3N$		R/S	µg/m^3
20	Output - Sample Conc. $(CH_3)_3N$			ppm
21	Input - Standard Conc. $(C_2H_5)_2NH$	µg/mℓ	R/S	
22	Input - Standard Area $(C_2H_5)_2NH$		R/S	
23	Input - Sample Area $(C_2H_5)_2NH$		R/S	
24	Output - Sample Conc. $(C_2H_5)_2NH$		R/S	µg/m^3
25	Output - Sample Conc. $(C_2H_5)_2NH$			ppm
26	Input - Standard Conc. $(C_2H_5)_3N$	µg/mℓ	R/S	
27	Input - Standard Area $(C_2H_5)_3N$		R/S	
28	Input - Sample Area $(C_2H_5)_3N$		R/S	
29	Output - Sample Conc. $(C_2H_5)_3N$		R/S	µg/m^3
30	Output - Sample Conc. $(C_2H_5)_3N$			ppm
			h RTN	

Figure 7. HP-67 user instructions.

STEP	KEY ENTRY	KEY CODE	COMMENTS	STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	Input Sample Vol, ft^3		x	71	Out Conc $\mu g/m^3$ $(CH_3)_3N$
	1	01			R/S	84	
	•	83			2	02	
	5	05		060	4	04	
	0	00			5	05	
	0	00			9	09	
	x	71			÷	81	
	R/S	84	Input Barometer, "Hg		R/S	84	Out Conc ppm $(CH_3)_3N$ In Std Conc $\mu g/ml$ $(C_2H_5)_2NH$
	x	71			RCL 2	34 02	
010	STO 1	33 01			x	71	
	R/S	84	Input Sample Temp, °F		R/S	84	In Std Area $(C_2H_5)_2NH$
	4	04			÷	81	
	6	06			R/S	84	In Samp Area $(C_2H_5)_2NH$
	0	00			x	71	
	+	61			R/S	84	Out Conc $\mu g/m^3$ $(C_2H_5)_2NH$
	RCL 1	34 01			3	03	
	h x⇄y	35 52			0	00	
	÷	81			4	04	
	h 1/x	35 62			2	02	
020	R/S	84	Input Dilution Factor		÷	81	
	x	71			R/S	84	Out Conc ppm $(C_2H_5)_2NH$
	R/S	84	Input Abs Sol Vol, ml		RCL 2	34 02	In Std Conc $\mu g/ml$ $(C_2H_5)_3N$
	x	71			x	71	
	STO 2	33 02		080	R/S	84	In Std Area $(C_2H_5)_3N$
	R/S	84	In Std Conc $\mu g/ml$ CH_3NH_2		÷	81	
	RCL 2	34 02			R/S	84	In Samp Area $(C_2H_5)_3N$
	x	71			x	71	
	R/S	84	In Std Area CH_3NH_2		R/S	84	Out Conc $\mu g/m^3$ $(C_2H_5)_3N$
	÷	81			4	04	
030	R/S	84	In Samp Area CH_3NH_2		2	02	
	x	71			0	00	
	R/S	84	Out Conc $\mu g/m^3$ CH_3NH_2		9	09	
	1	01			÷	81	
	2	02		090	R/S	84	Out Conc ppm $(C_2H_5)_3N$
	•	83			h RTN	35 22	
	2	02					
	÷	81					
	R/S	84	Out Conc ppm CH_3NH_2				
	RCL 2	34 02	In Std Conc $\mu g/ml$ CH_3NH_2				
040	x	71					
	R/S	84	In Std Area C_2H_7N				
	÷	81					
	R/S	84	In Samp Area C_2H_7N				
	x	71		100			
	R/S	84	Out Conc $\mu g/ml$ C_2H_7N				
	1	01					
	8	08					
	7	07					
	5	05					
050	÷	81	Out Conc ppm C_2H_7N				
	R/S	84	In Std Conc $\mu g/ml$ $(CH_3)_3N$				
	RCL 2	34 02					
	x	71					
	R/S	84	In Std Area $(CH_3)_3N$				
	÷	81					
	R/S	84	In Samp Area $(CH_3)_3N$				

REGISTERS

Figure 7 (Cont'd). HP-67 program form.

SWRI PROJECT NO.__________TEST NO.__________TEST DATE:__________VEHICLE:__________

FUEL:_______CVS NO.________TUNNEL SIZE:________DRIVER:__________MILES:__________

SAMPLE COLLECTION BY:__________CHEMICAL ANALYSIS BY:______CALCULATIONS BY:_______

GENERAL COMMENTS:____

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-2	FTP-3	SET-7	HFET	NYCC
Volume Ft^3	3.196	1.625	2.010	3.730	8.241	1.070
B.P." Hg	29.80	30.02	29.02	29.25	29.95	29.50
Temp°F	75	80	96	85	83	89
Dilution Factor	1	5	10	2	1	1
Absorb. Rea. Vol. Ml	25	25	50	50	75	75
Stan. Conc. CH_3NH_2 μg/ml	0.05	0.10	0.02	1.00	0.10	0.10
Stan. Area CH_3NH_2	1000	2000	3000	10000	4000	5000
Sample Area CH_3NH_2	640	1000	1880	800	2000	2700
Sample Conc. CH_3NH_2 μg/m^3	8.99	138	119	79.9	16.5	141
Sample Conc. CH_3NH_2 ppm	0.007	0.107	0.092	0.062	0.013	0.109
Stan. Conc. C_2H_7N μg/ml	0.10	0.20	0.30	2.00	0.20	0.20
Stan. Area C_2H_7N	1500	3000	6000	15000	2000	3000
Sample Area C_2H_7N	1000	1800	5000	8500	1500	2000
Sample Conc. C_2H_7N μg/m^3	18.7	332	2380	1130	49.5	348
Sample Conc. C_2H_7N ppm	0.010	0.177	1.270	0.603	0.026	0.186
Stan. Conc. $(CH_3)_3N$ μg/ml	0.50	1.00	0.20	2.00	1.50	1.00
Stan. Area $(CH_3)_3N$	1500	3000	4000	2000	1000	2000
Sample Area $(CH_3)_3N$	1020	2800	2100	1600	875	1630
Sample Conc. $(CH_3)_3N$ μg/m^3	95.5	2580	1000	1600	433	2130
Sample Conc. $(CH_3)_3N$ ppm	0.039	1.050	0.407	0.650	0.176	0.865
Stan. Conc. $(C_2H_5)_2NH$ μg/ml	0.90	1.50	0.10	1.00	0.50	0.40
Stan. Area $(C_2H_5)_2NH$	1560	3000	1870	1420	1900	3100
Sample Area $(C_2H_5)_2NH$	1760	4321	2000	1070	1870	2810
Sample Conc. $(C_2H_5)_2NH$ μg/m^3	285	5980	1020	753	162	946
Sample Conc. $(C_2H_5)_2NH$ ppm	0.094	1.970	0.335	0.247	0.053	0.311
Stan. Conc. $(C_2H_5)_3N$ μg/ml	1.60	2.00	0.10	0.50	0.60	0.20
Stan. Area $(C_2H_5)_3N$	3120	1260	4000	6210	3110	5620
Sample Area $(C_2H_5)_3N$	2850	780	3160	3100	2000	4020
Sample Conc. $(C_2H_5)_3N$ μg/m^3	410	3430	753	249	127	373
Sample Conc. $(C_2H_5)_3N$ ppm	0.098	0.814	0.179	0.059	0.030	0.089

Figure 8. Organic amine sample collection sheet.

Manual calculations for driving cycle FTP-1

$$\mu g/m^3\ CH_3NH_2 = \frac{C_{std}(\mu g/m\ell) \times A_{sam} \times D.F. \times Abs.\ Vol.\ (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg})}$$

$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528°R \times V_{exp}\ (ft^3)}$$

$$= \frac{(0.05\ \mu g/m\ell) \times 640 \times 1 \times 25}{1000 \times 29.80\text{"Hg}}$$

$$\times \frac{(460 + 75) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528°R \times 3.196\ ft^3}$$

$$= 8.99\ \mu g/m^3$$

$$PPM\ CH_3NH_2 = \mu g/m^3 \div density\ \mu g/m\ell$$

$$density\ \mu g/m\ell = \frac{Mol.\ Wt.\ (CH_3NH_2) \times 1000}{24.04\ell}$$

$$Mol.\ Wt.\ CH_3NH_2 = 31.058\ g/mole$$

$$density = \frac{31.058 \times 1000}{24.04\ell} = 1292\ \mu g/m\ell$$

$$ppm = 8.99\ \mu g/m^3 \div 1292\ \mu g/m\ell = 0.007\ m\ell/m^3 = 0.007\ ppm$$

The calculation for C_2H_7N, $(CH_3)_3N$, and $(C_2H_5)_3N$ are carried out in the same manner by substituting the appropriate standard concentrations, areas and molecular weights into the above formulas. These calculations give the following concentrations: C_2H_7N, 18.7 $\mu g/m^3$ and 0.01 ppm; $(CH_3)_3N$, 0.05 $\mu g/m^3$ and 0.039 ppm; $(C_2H_5)NH$, 285 $\mu g/m^3$ and 0.094 ppm; and $(C_2H_5)_3N$, 410 $\mu g/m^3$ and 0.098 ppm.

Note: The values used in these calculations are picked from a range of temperature, standards, dilution factors, etc., to validate the calculations and may not be representative of expected raw data. These calculations are presented to confirm the manual and HP-67 calculations give the same results. This was confirmed on six sets of calculations.

LIST OF EQUIPMENT AND REAGENTS

The equipment and reagents for the analysis of the organic amines are divided into two groups. The first involves the sample acquisition and the second the instrumental analysis of the sample once it has been obtained. Manufacturer, stock number and any pertinent descriptive information are listed. The preparation of the absorbing solution, the ascarite pre-column and the primary standards are also discussed.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.
2. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range.
3. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/min.
4. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.
5. Regulating valve, Nupro 4MG, stainless steel.
6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 1/8" ID.
7. Teflon solenoid valve, the Fluorocarbon Company, Model DV2-144NCA1.
8. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.
9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.
10. Digital readout for dry gas meter.
11. Miscellaneous electrical switches, lights, wirings, etc.
12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.
13. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.
14. 30 mℓ polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.
15. Sulfuric Acid, H_2SO_4, formula weight - 98.08, Certified 1 N by Fisher Scientific Company, #SO-A-212.

16. Class A, 10 mℓ volumetric pipet.

17. Class A, 1000 mℓ volumetric flask.

18. Stainless steel heated filter assembly - 7 cm, Scott, capable of temperatures to 204°C, includes 2 heated, adjustable thermostat switch, stainless steel insulated covers and sample bypass solenoid valves.

19. Glass microfiber filter discs, Reeve Angel 934-AH, Whatman, 7 cm diameter.

20. Flexible, heavy insulation heating tape, Briskeat®, width - 1/2 inch, length - 48 inches.

21. Temperature Controller, Athena, 100-600°F.

22. Heated TFE Teflon hose, Technical Heaters Inc., 5' x 1/4", temperature limit 400°F.

Instrumental Analysis

1. 10 µl syringe, Pressure-Lok, Precision Sampling Corporation.

2. Perkin-Elmer Model 3920 B gas chromatograph equipped with an ascarite loaded pre-column, a Teflon interface, and a nitrogen phosphorus detector (NPD).

3. Soltec Model B-281 mv recorder.

4. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout.

5. Glass insert for 1/8" and 1/4" heated injectors (used as pre-column), Perkin-Elmer, #009-1958.

6. Ascarite, 20-30 mesh, Arthur H. Thomas Company, Catalog #C049-U86.

7. Teflon tubing (used for interface in gas chromatograph), Analabs Inc., 1/6" OD x 0.03" ID, #HGC-024.

8. Methylamine Hydrochloride, $CH_3NH_2 \cdot HCl$, formula weight = 67.52, crystals, Eastman #116.

9. Dimethylamine Hydrochloride, $(CH_3)_2NH \cdot HCl$, formula weight = 81.55, crystals, Eastman #94.

10. Trimethylamine Hydrochloride, $(CH_3)_3N \cdot HCl$, formula weight = 95.57, crystals, Eastman #265.

11. Ethylamine Hydrochloride, $C_2H_5NH_2 \cdot HCl$, formula weight = 81.55, crystals, Eastman #731.

12. Diethylamine Hydrochloride, $(C_2H_5)_2NH \cdot HCl$, formula weight = 109.6, crystals, Eastman #2090.

13. Triethylamine Hydrochloride, $(C_2H_5)_3N \cdot HCl$, formula weight = 137.65, crystals, Eastman #8535.

Preparation of Absorbing Solution

The absorbing solution (0.01 N H_2SO_4) is prepared by diluting 10 mℓ of 1 N sulfuric acid (certified Fisher Scientific Company) to 1 liter with deionized water.

Preparation of Ascarite Pre-Column

The ascarite pre-column is prepared by packing a Perkin-Elmer glass insert for a heated injector block with 20-30 mesh ascarite and plugging both ends with 1/4" of glass wool. The packed pre-column is shown in Figure 4. This packed pre-column is then inserted into the heated injector and held in place against the column with a spring loaded metal tube and the septum cap.

Preparation of Primary Standards

The primary standards for the organic amines are prepared by dissolving a weighed amount of the amine-hydrochloric acid salt in 0.01 N sulfuric acid and diluting the resulting mixture to the proper volume with 0.01 N sulfuric acid. Standards less than 10 ppm are prepared by diluting higher concentration standards with 0.01 N sulfuric acid.

REFERENCES

Braker, W. and Mossman, A. L., Matheson Gas Data Book, 5th Edition, East Rutherford, N. J., 1971, pg. 385.

Weast, R. C., (Ed.), Handbook of Chemistry and Physics, 54th Edition, The Chemical Rubber Co., Cleveland, Ohio, 1973.

Hoshika, Y., Anal. Chem., Vol. 48, pg. 1716, 1976.

Hoshika, Y., J. Chromatog., Vol. 115, pg. 596, 1975.

Sze, Y. L. and Borke, M. L., Anal. Chem., Vol. 35, pg. 240, 1963.

O'Donnell, J. F., and Mann, C. K., Anal. Chem., Vol. 36, pg. 2097, 1964.

McCurdy, W. H. Jr., and Reiser, R. W., Anal. Chem., Vol. 38, pg. 795, 1966.

Smith, J. R. L. and Waddington, D. J., Anal. Chem., Vol. 40, pg. 522, 1977.

"Amine Analysis," Bulletin 737A, Supelco Co., Belefonte, Pa., 1973.

"Penwalt 223 Amine Packing," Alltech Assoc., Arlington Heights, Illinois.

Moffat, A. C. and Horning, E. C., Anal. Lett., Vol. 3, pg. 205, 1970.

Clarke, D. D., Wilk, S., and Gitlow, S. E., J. Gas Chromatog., pg. 310, 1966.

Mosier, A. R., Andre, C. E., and Viets, F. G. Jr., Environ. Sci. Tech., Vol. 7, pg. 642, 1973.

Burks, R. E. Jr., Baker, E. B., Clark, P., Esslinger, J., Lacey, J. C. Jr., J. Agr. Food Chem., Vol. 7, pg. 778, 1959.

Dunn, S. R., Simehoff, M. L., Wesson, L. G. Jr., Anal. Chem., Vol. 48, pg. 41, 1976.

Gruger, E. H. Jr., J. Agr. Food Chem., Vol. 20, pg. 781, 1972.

Andre, C. E. and Mosier, A. R., Anal. Chem., Vol. 45, pg. 1971, 1973.

Umbreit, G. R., Nygren, R. E., and Testa, A. J., J. Chromatog., Vol. 43, pg. 25, 1969.

Keay, J. N. and Hardy, R., J. Sci. Food Agr., Vol. 23, pg. 9, 1972.

Bowen, B. E., Anal. Chem., Vol. 48, pg. 1584, 1976.

APPENDIX E

SULFUR DIOXIDE PROCEDURE

THE MEASUREMENT OF SULFUR DIOXIDE IN EXHAUST

The concentration of sulfur dioxide, SO_2, in automotive exhaust can be determined as sulfate using an ion chromatograph. Sulfur dioxide exhaust samples are collected in two glass bubblers, each containing 3 percent hydrogen peroxide. The temperature of the absorbing solution is kept at 0°C by means of an ice water bath. The bubbled samples are analyzed on the ion chromatograph and compared to standards of known sulfate concentrations.

SAMPLING SYSTEM

Two glass impingers in series, each containing 25 mℓ of a 3 percent hydrogen peroxide solution, are used to collect exhaust samples for the analysis of sulfur dioxide. A flow schematic of the sample collection system is shown in Figure 1. The two impingers together trap approximately 99 percent of the sulfur dioxide. The temperature of the impinger is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4 ℓ/minute by the sample pump. A dry gas meter is used to determine the total flow through the impinger during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allows continuous monitoring of the sample flow to insure proper flow rates during sampling. When sampling diesel fueled vehicles, a heated filter, located between the on-off solenoid valve and the dilution tunnel, is used to prevent diesel particulate from contaminating the sampling system. The filter and line connecting the filter to the dilution tunnel are heated to 375°F in order to prevent sulfur dioxide from being retained in the filter and sample line. The Teflon line connecting the heated filter and the solenoid valve is heated to 175°F in order to prevent water from condensing in the sample line. Several views of the sampling system are shown in Figure 2.

ANALYTICAL PROCEDURE

Sulfur dioxide in dilute exhaust is collected in two impingers connected in series with each impinger containing 25 mℓ of 3 percent hydrogen peroxide. The temperature of the impinger is maintained at 0-5°C by an ice water bath. The flowrate through the impinger is adjusted to 4 ℓ/minute with a regulating valve and the sample pump. After sampling is completed, the absorbing solution in each bubbler is transferred to a 30 mℓ polypropylene bottle and capped. The samples should be analyzed within four or five weeks after collection. Approximately 2 mℓ of the sample is loaded into the ion chromatograph sample loop and injected. The injection inserts the sample loop volume (0.5 mℓ) of sample into the instrument. An analysis flow schematic and pictures of the ion chromatograph are shown in Figures 3 and 4. The ion chromatograph

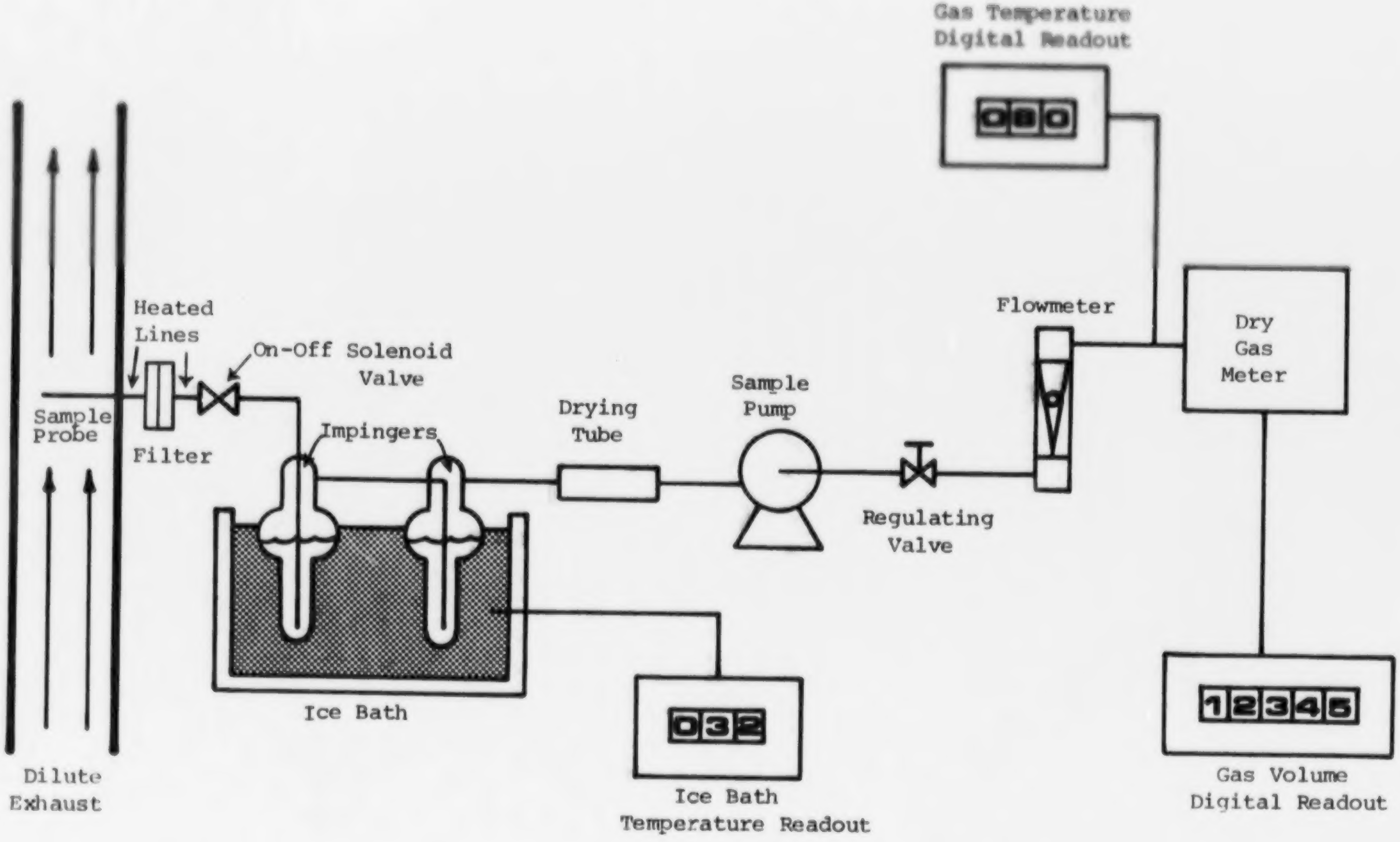
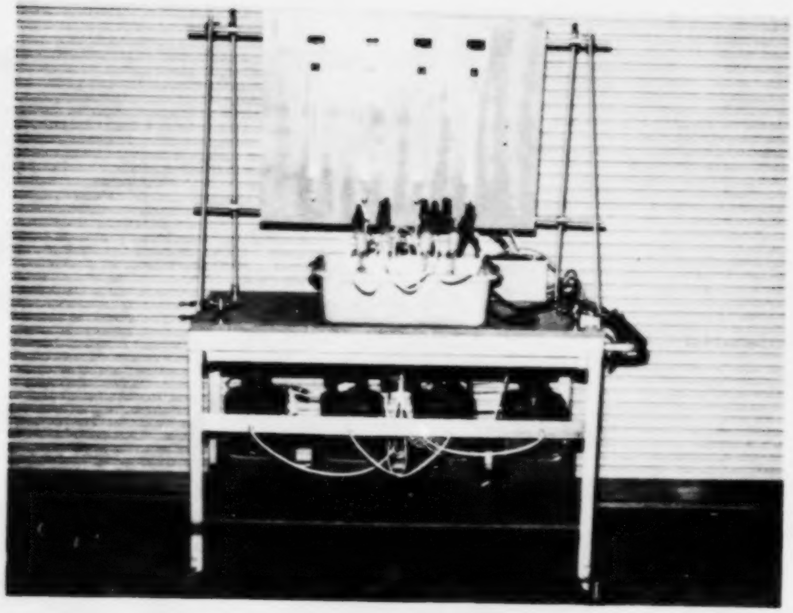
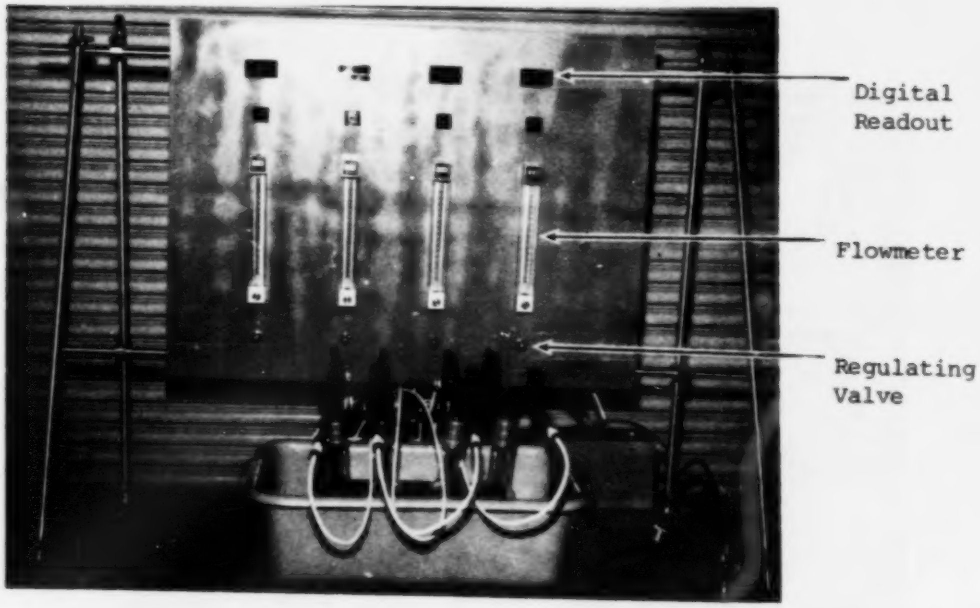

Gas Temperature
Digital Readout
080
Heated
Lines
On-Off Solenoid
Valve
Sample
Probe
Filter
Impingers
Drying
Tube
Sample
Pump
Regulating
Valve
Flowmeter
Dry
Gas
Meter
Ice Bath
Dilute
Exhaust
032
Ice Bath
Temperature Readout
12345
Gas Volume
Digital Readout

Figure 1. SO_2 sample collection flow schematic.



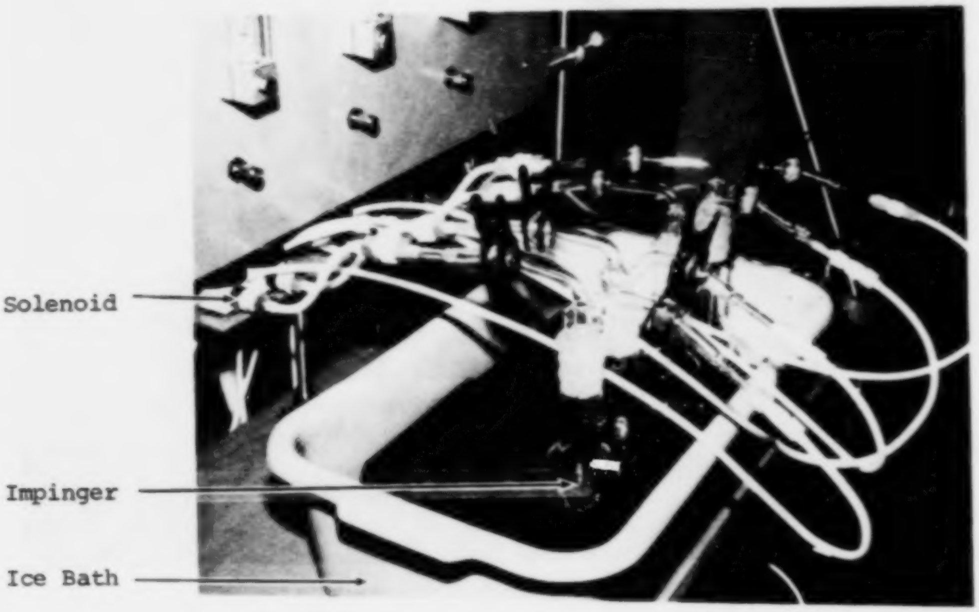
Front View



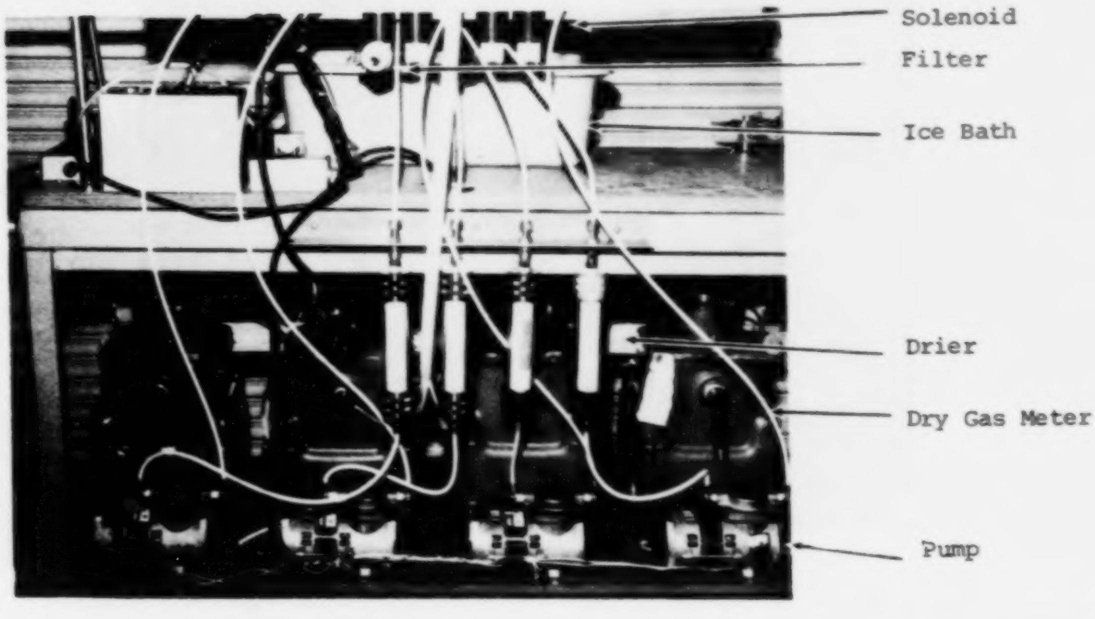
Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. SO_2 sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). SO_2 sampling system.

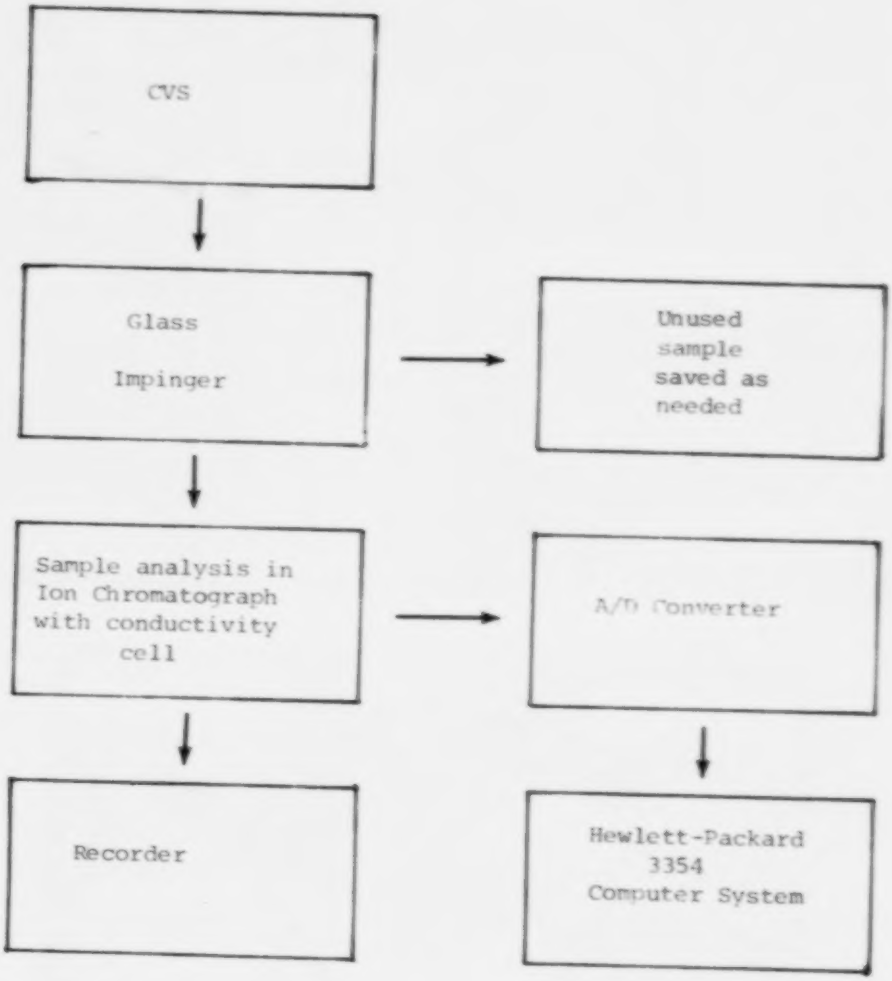

CVS
Glass Impinger
Unused sample saved as needed
Sample analysis in Ion Chromatograph with conductivity cell
A/D Converter
Recorder
Hewlett-Packard 3354 Computer System

Figure 3. SO_2 analysis flow schematic.

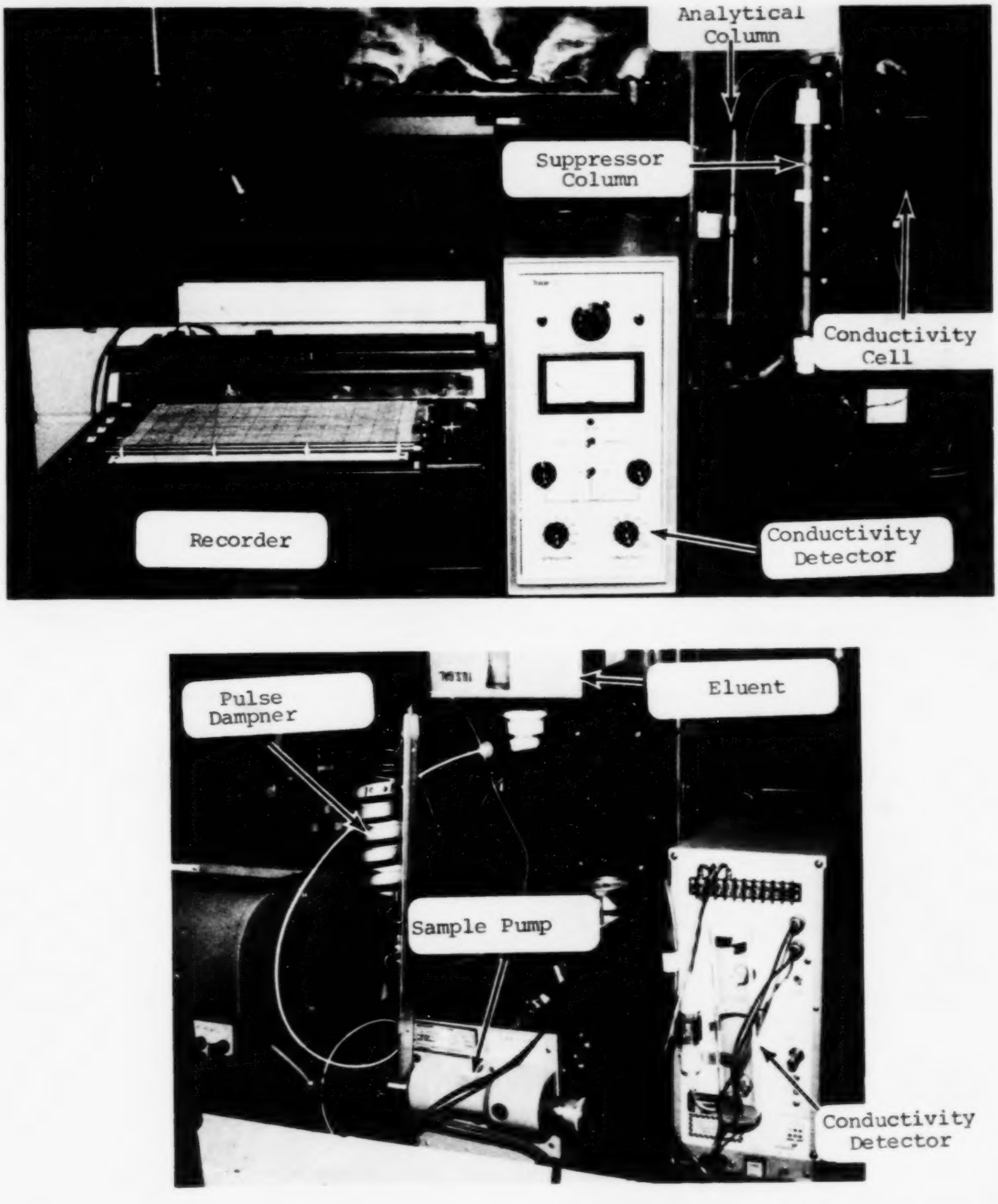

Analytical Column
Suppressor Column
Conductivity Cell
Recorder
Conductivity Detector
Pulse Dampner
Eluent
Sample Pump
Conductivity Detector

Figure 4. SO_2 ion chromatograph.

utilizes two columns, the separator and the suppressor. The 3 x 500 mm analytical column and a 3 x 150 mm precolumn are packed with a patented resin composed of a strong base anion exchanger in the bicarbonate form. The analytical column separates the anions before entering the suppressor column. The 6 x 250 mm glass suppressor column packed with AG 50W-X10, a strong acid cation exchanger, neutralizes the ionic effect of the eluent while increasing that of the sample ion. The column packing is in the hydrogen form so that in the presence of the eluent ($NaHCO_3$ and Na_2CO_3), H_2CO_3 is generated and when sulfate is introduced, H_2SO_4 is formed.

$$NaHCO_3 + \text{Resin-H} \rightleftharpoons \text{Resin-Na} + H_2CO_3$$

$$Na^+ \text{ Anion}^- + \text{Resin-H} \rightleftharpoons \text{Resin-Na} + H^+ \text{ Anion}^-$$

The acid being more conductive than the hydrogen carbonate produces a signal on the conductivity meter. This can be interpreted as peak height from a trace or as peak area measured by the Hewlett-Packard 3354 computer system. Figures 5 and 6 show two representative chromatograms produced in the analysis of a standard and a sample. The ion chromatograph operates at room temperature at a maximum pressure of 500 psi.

CALCULATIONS

This procedure has been developed to provide the user with the concentration of sulfur dioxide in exhaust. The results will be expressed in $\mu g\ SO_2/m^3$ of exhaust and ppm. A stepwise derivation of the equations used in calculating the concentrations is provided as well as a copy of a Hewlett-Packard 67 calculator program (Figure 7). This program is designed to reduce the amount of time required to do the calculations manually. For illustration, two examples using information from the data sheet (Figure 8) are included at the end of this section.

The first step in the calculations is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92" Hg, by use of the equation:

$$\frac{PxVx}{Tx} = \frac{Pspec \times V}{Tspec}$$

Solving for V gives:

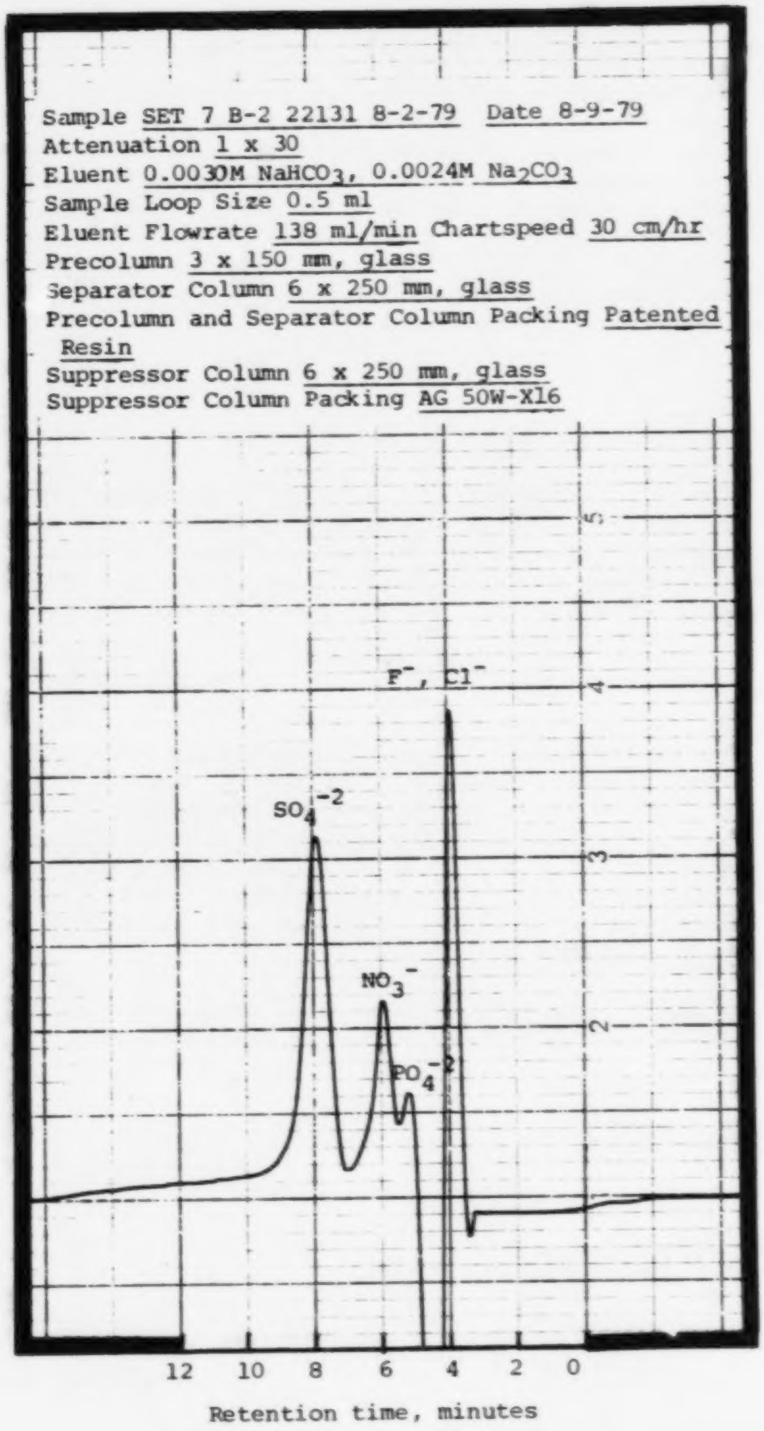
$$V = \frac{PxVx}{Tx+460} \times \frac{Tspec}{Pspec}$$

where V = volume of gas sampled at specified temperature and pressure (ft^3)

Px = experimental pressure ("Hg)

Vx = experimental gas volume collected (ft^3)

Tx = experimental temperature (°F)



Sample SET 7 B-2 22131 8-2-79 Date 8-9-79

Attenuation 1 x 30

Eluent 0.0030M $NaHCO_3$, 0.0024M Na_2CO_3

Sample Loop Size 0.5 ml

Eluent Flowrate 138 ml/min Chartspeed 30 cm/hr

Precolumn 3 x 150 mm, glass

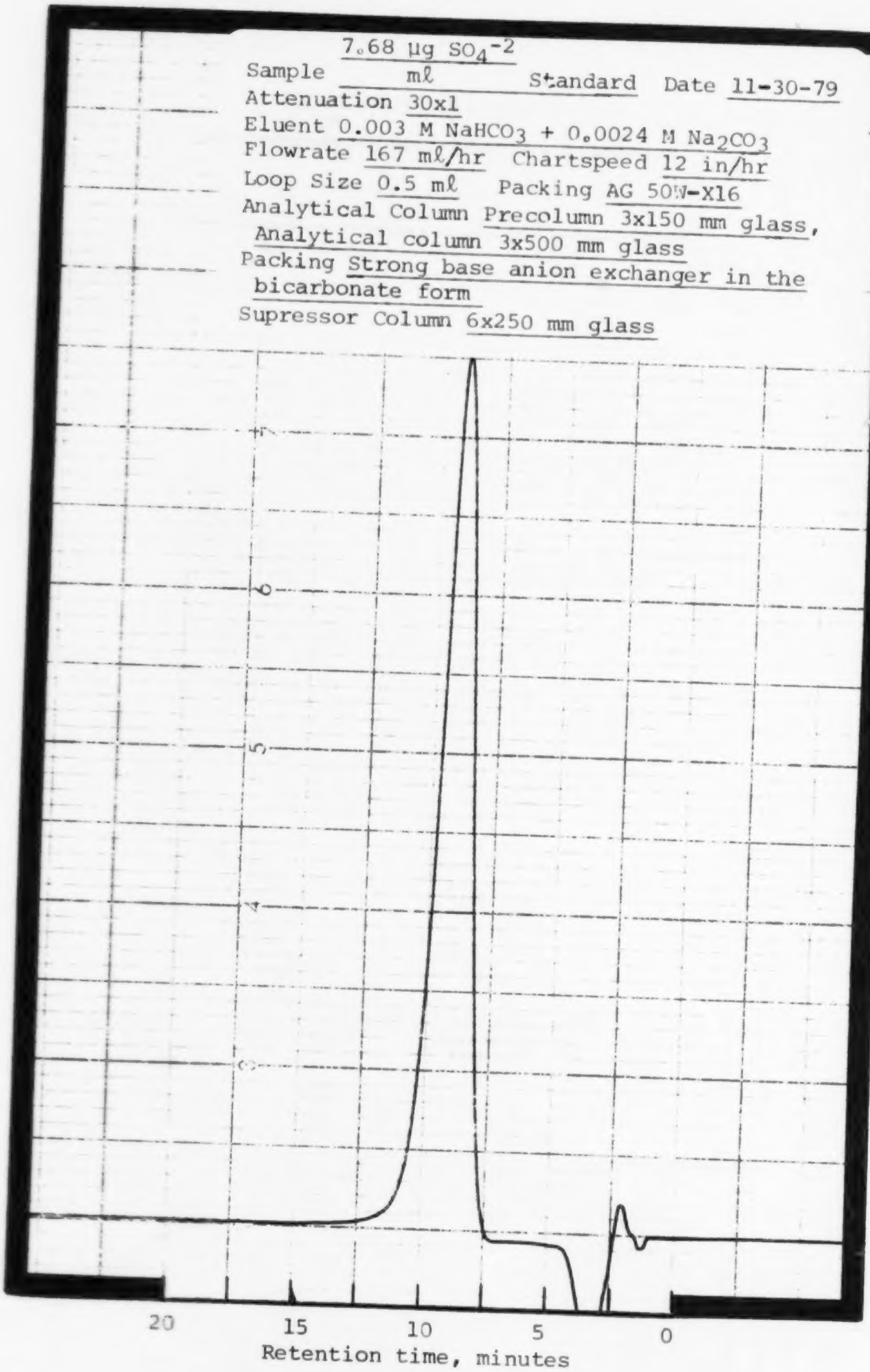
Separator Column 6 x 250 mm, glass

Precolumn and Separator Column Packing Patented Resin

Suppressor Column 6 x 250 mm, glass

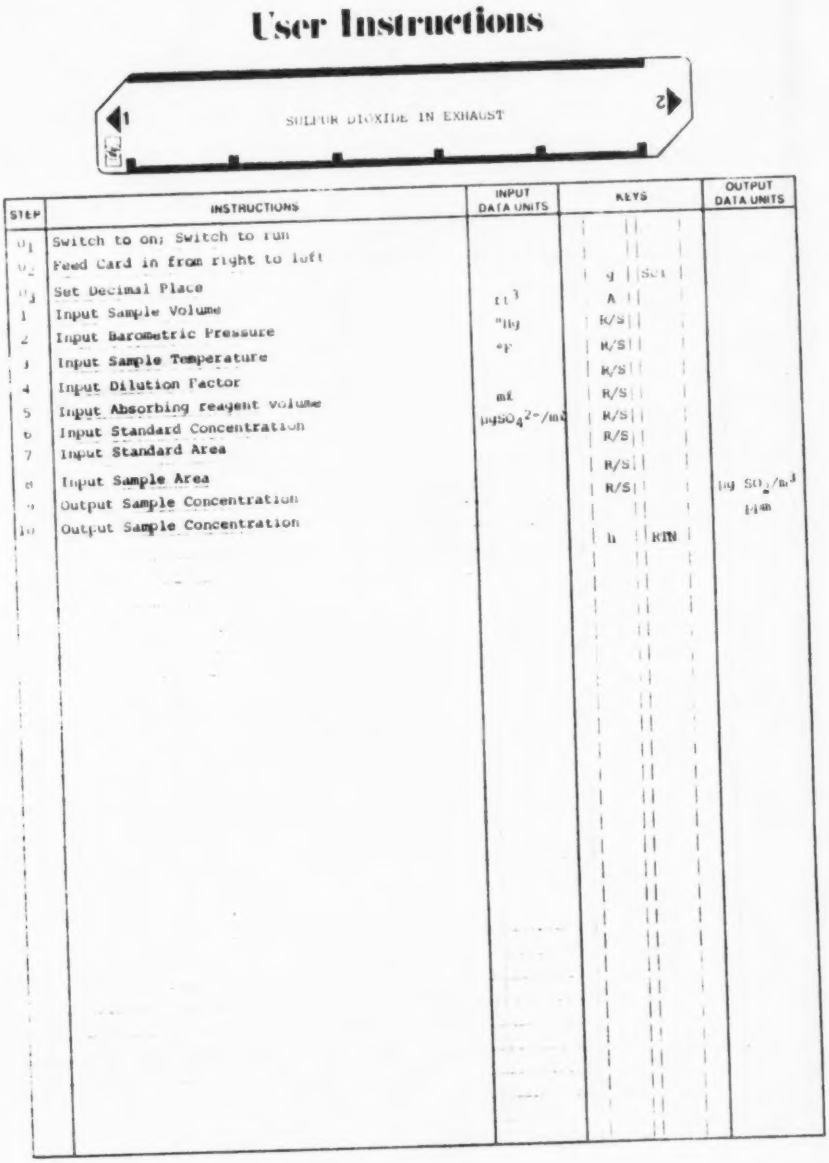
Suppressor Column Packing AG 50W-X16

Figure 5. Sample chromatogram.



Sample $7.68\ \mu g\ SO_4^{-2}$ mℓ Standard Date 11-30-79
Attenuation 30x1
Eluent 0.003 M $NaHCO_3$ + 0.0024 M Na_2CO_3
Flowrate 167 mℓ/hr Chartspeed 12 in/hr
Loop Size 0.5 mℓ Packing AG 50W-X16
Analytical Column Precolumn 3x150 mm glass, Analytical column 3x500 mm glass
Packing Strong base anion exchanger in the bicarbonate form
Supressor Column 6x250 mm glass

Figure 6. Standard Chromatogram



User Instructions

SULFUR DIOXIDE IN EXHAUST

STEP	INSTRUCTIONS	INPUT DATA UNITS	KEYS	OUTPUT DATA UNITS
01	Switch to on; Switch to run			
02	Feed Card in from right to left			
03	Set Decimal Place		g Set	
1	Input Sample Volume	ft^3	A	
2	Input Barometric Pressure	"Hg	R/S	
3	Input Sample Temperature	°F	R/S	
4	Input Dilution Factor		R/S	
5	Input Absorbing reagent volume	ml	R/S	
6	Input Standard Concentration	$\mu g SO_4^{2-}/ml$	R/S	
7	Input Standard Area		R/S	
8	Input Sample Area		R/S	
9	Output Sample Concentration		R/S	$\mu g\ SO_2/m^3$
10	Output Sample Concentration		h RTN	ppm

Figure 7. HP-67 user instructions.

STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	Input Sample Vol, ft^3
	3	03	
	5	05	
	.	83	
	3	03	
	1	01	
	÷	81	
	5	05	
	2	02	
010	8	08	
	X	71	
	2	02	
	9	09	
	.	83	
	9	09	
	2	02	
	÷	81	
	R/S	84	Input Barometer,"Hg
	X	71	
020	STO 01	33 01	
	R/S	84	Input Sample Temp, °F
	4	04	
	6	06	
	0	00	
	+	61	
	RCL 1	34 01	
	h X ⇄ Y	35 52	
	÷	81	
	h 1/X	35 62	
030	R/S	84	Input Dilution Factor
	X	71	
	R/S	84	Input Abs Soln Vol, mℓ
	X	71	
	R/S	84	Input Std Conc
	X	71	μg SO_4^{2-}/mℓ
	R/S	84	Input Std Area
	÷	81	
	R/S	84	Input Sample Area
	X	71	
040	0	00	
	.	83	
	6	06	
	6	06	
	7	07	
	X	71	
	R/S	84	Output Conc, μg SO_2/m^3
	0	00	
	.	83	
	0	00	
050	0	00	
	0	00	
	3	03	
	6	06	
	7	07	
	X	71	
	R/S	84	Output Conc, ppm SO_2

STEP	KEY ENTRY	KEY CODE	COMMENTS
	h RTN	35 22	
060			
080			
090			
100			
110			

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9
A	B	C	D	E	I				

Figure 7 (Cont'd). HP-67 program form.

SwRI Project No. ____________ Test No. _____ Test Date: ____________ Vehicle: ____________
Fuel: ____________ CVS No. _____ Tunnel Size ________ Driver: ____________ Miles: ________
Sample Collection By: _______ Chemical Analysis By: ______________ Calculations By: ________
General Comments: ____

Driving Cycle	Sampling Conditions			Dilution Factor	Absorb. Reagent Volume mℓ	Standard		Sample		
	Volume Ft^3	B.P. "Hg	Temp. °F			$\mu g SO_4^{-2}/m\ell$	Area	Area	$\mu g SO_2/m^3$	ppm
FTP-1	1.189	29.47	74.7	1	25	10	3200	4000	6360	2.34
FTP-2	2.040	29.48	75.0	1	25	30	4500	3500	6930	2.54
FTP-3	1.250	29.49	74.5	1	25	10	3200	4300	6500	2.39
SET-7	3.240	29.50	75.0	1	25	40	4200	4500	8000	2.94
HFET	1.690	29.50	74.7	1	25	20	5700	5500	6670	2.45
NYCC	1.410	29.51	74.9	1	25	15	4900	5000	6630	2.43
BG	2.000	29.45	74.9	1	25	1.0	3000	2700	273	0.10
	1	2	3	4	5	6	7	8	9	10

Figure 8. SO_2 data sheet.

Tspec = specified temperature = 68°F = 528°R

Pspec = specified pressure = 29.92 " Hg

Next, the quantity of SO_2 in this volume of gas is calculated. The ion chromatograph measures the amount of sulfate (from SO_2) in $\frac{\mu g\ SO_4^{-2}}{m\ell}$. Assuming linearity between concentration of sulfate and peak area, a standard of known sulfate concentration is compared to a bubbled exhaust sample.

$$\frac{Cst}{AREAst} = \frac{Csamp}{AREAsamp}$$

$$Csamp = \frac{Cst \times AREAsamp}{AREAst}$$

where Csamp = concentration of SO_4^{-2} in sample $\frac{\mu g\ SO_4^{-2}}{m\ell}$

Cst = concentration of SO_4^{-2} in standard $\frac{\mu g\ SO_4^{-2}}{m\ell}$

AREAsamp = area of sample (relative units)

AREAst = area of standard (relative units)

Converting to $\mu g\ SO_2/m\ell$:

$$Csamp \times \frac{64.06\ g/mole\ SO_2}{96.06\ g/mole\ SO_4^{-2}} = 0.667\ Csamp$$

If the sample has been diluted the dilution factor, DF, needs to be included.

$$0.667\ Csamp \times DF$$

This represents the amount of SO_2 in one mℓ of absorbing solution. The volume of absorbing solution is multiplied by this last quantity to give the amount of SO_2 collected.

$$0.667\ Xsamp \times DF \times absorb.\ vol.\ (m\ell) = \mu g\ SO_2$$

The concentration of SO_2 in $\frac{\mu g\ SO_2}{m^3}$ in the exhaust sample is obtained by dividing $\mu g\ SO_2$ by gas volume (corrected from ft^3 to m^3).

Concentration of SO_2, $\dfrac{\mu g\ SO_2}{m^3}$ =

$$\frac{0.667\ \dfrac{\mu g\ SO_2}{\mu g\ SO_4^{-2}} \times \dfrac{\text{Cst},\ \dfrac{\mu g\ SO_4^{-2}}{m\ell} \times \text{AREAsamp}}{\text{AREAst}} \times \text{DF} \times \text{absorb. vol., } m\ell}{\dfrac{\text{Px, "Hg x Vx, ft}^3}{\text{Tx, °F + 460}} \times \dfrac{528°R}{29.92"\ Hg}}$$

$$= \frac{0.667\ \dfrac{\mu g\ SO_2}{\mu g\ SO_4^{-2}} \times \text{Cst},\ \dfrac{\mu g\ SO_4^{-2}}{m\ell} \times \text{AREAsamp} \times \text{DF} \times \text{absorb. vol., } m\ell}{\text{Px, "Hg x Vx, ft}^3} \times$$

$$\frac{(\text{Tx, °F + 460}) \text{ x } 29.92"\ Hg \times 35.31\ \dfrac{m^3}{ft^3}}{528°R \times \text{AREAst}}$$

To find the SO_2 concentration in ppm the density of the gas at the specified conditions is needed. The density of SO_2 at 32°F and 29.92" Hg is 2.927 g/lit. This can be corrected to 68°F (492°R) and 29.92" Hg using Charles' version of the ideal gas law:

$$\frac{V}{T} = \frac{V_1}{T_1}$$

where V_1 is the volume at 32°C (ℓ) = 1.0 ℓ
T_1 is 32°F = 492°R
V is the volume at 68°F (ℓ)
T is 68°F - 528°R

$$V = \frac{(1.0\ \ell)\ (528°R)}{492°R} = 1.073\ \ell$$

Density at 68°F and 29.92" Hg $= \dfrac{2.927\ g}{1.073\ \ell}$

$$= 2.728\ g/\ell = 2728\ \frac{\mu g}{m\ell}$$

$$= 0.000367\ \frac{m\ell}{\mu g}$$

$$\frac{\mu g\ SO_2}{m^3} \times 0.000367\ \frac{m\ell}{\mu g} = \frac{m\ell}{m^3} = \text{ppm } SO_2$$

Sample Calculation

The two examples will be calculated from information recorded on the data sheet (Figure 8). This information does not necessarily represent actual experimental data but serves as a means of confirming calculations done by hand with those done with the Hewlett-Packard Calculator.

Example 1

Assume 1.189 ft^3 of exhaust was collected in 25 $m\ell$ of 3 percent H_2O_2 in the FTP-1 driving cycle at a barometric pressure of 29.47" Hg (corrected) and temperature of 74.7°F. The sampling and analysis were both performed according to the procedure outlined in a previous section. An excess of sample injected into the 0.5 $m\ell$ sample loop produced a peak area of 4000 counts and the corresponding standard, $\frac{10\ \mu g\ SO_4^{-2}}{m\ell}$, an area of 3200 count.

$$\mu g\ SO_2/m^3 = \frac{0.667\ \frac{\mu g\ SO_2}{\mu g\ SO_4^{-2}} \times Cst,\ \frac{\mu g\ SO_4^{-2}}{m\ell} \times AREAsamp}{Px,\ "Hg \times Vx,\ ft^3} \times$$

$$\frac{DF \times absorb.\ vol.,\ m\ell \times (Tx,\ °F + 460) \times 29.92"\ Hg \times 35.31\ \frac{m^3}{ft^3}}{528°R \times AREAst}$$

$$= \frac{0.000367 \times 0.667 \times 10 \times 4000 \times 1 \times 25 \times (74.7 + 460) \times 29.92 \times 35.31}{29.47 \times 1.189 \times 528 \times 3200}$$

$$= 6360\ \mu g\ SO_2/m^3$$

$$ppm\ SO_2 = 6360\ \mu g\ SO_2/m^3 \times 0.000367\ \frac{m\ell}{\mu g\ SO_2}$$

$$= 2.34\ ppm\ SO_2$$

Example 2

Assume that in the SET-7 driving cycle dilute automotive exhaust was collected in 25 $m\ell$ of 3 percent H_2O_2 according to the procedure described previously. The sampling conditions under which the 3.240 ft^3 of exhaust was collected were 75.0°F and 29.50 " Hg. An area of 4200 counts was produced by the 40 $\frac{\mu g\ SO_4^{-2}}{m\ell}$ standard and the exhaust sample yielded an area of

4500 counts. Inserting these values into the same equation used in Example 1 gives concentrations of 8000 μg SO_2/m^3 and 2.94 ppm SO_2.

LIST OF EQUIPMENT

The equipment required for the SO_2 determination is divided into four categories: Sampling, Analysis, Water Filtration and Sample preparation. Manufacturer, stock number and any pertinent descriptive information are listed.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.
2. Flowmeters, Brooks Instrument Division, Model 1555, R-2-15-C, sapphire ball, 0-5 lit/min range, graduated 0-15.
3. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.
4. Digital readout for dry gas meter.
5. Sample pump, Thomas, Model #106 CA18 3, 4 lit/min.
6. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.
7. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 3/16" ID.
8. Teflon solenoid valve, The Fluorocarbon Company, Model #DV2-144N Cal.
9. Miscellaneous Teflon nuts, ferrules, unions, tees, connectors and clamps.
10. Miscellaneous electrical switches, lights, wiring, etc.
11. Regulating valve, Nupro 4M6, stainless steel.
12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.
13. 30 ml polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.
14. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.
15. Stainless steel heated filter assembly-7 cm; Scott, capable of temperature to 204°C, included 2 heaters, adjustable thermostat switch,

stainless steel insulated covers and sample bypass solenoid valves.

16. Glass microfiber filter discs, Reeve Angel 934-AH, Whatman, 7 cm diameter.

17. Flexible heavy insulation heating tape, Briskeat®, width-1/2 inch, length-48 inches.

18. Temperature Controller, Athena, 100-600°F.

19. Heated TFE Teflon hose, Technical Heaters, Inc., 5' x 1/4" temperature limit 400°F.

Analysis

1. Conductivity cell, modified swagelok reducing union, Catalog #SS-200-6-1, approximate volume, 4.5 μl.

2. Conductivity detector, Hall, Tracor 700.

3. Multivoltage recorder, Soltec, Model #B-281 H.

4. Mini-pump, Milton Roy, series 196-0066-033, 46/460 mℓ/hr capacity.

5. Pulse dampener, Glenco Scientific, Catalog #PD 1000.

6. Polyethylene cubitainers, Cole Parmer Instrument Company, Catalog #6100-20, 1 gallon.

Water Filtration

1. Filtration apparatus, Millipore, Catalog #XX 15 047 00.

2. Filters, Millipore, Catalog #GSWP 047 00, 0.22 micron pore size.

Sample preparation

1. 3 cc disposable syringes, Becton-Dickson, Catalog #5585.

2. Class A, 1 mℓ volumetric pipets.

3. Class A, 2 mℓ volumetric pipets.

4. Class A, 3 mℓ volumetric pipets.

5. Class A, 4 mℓ volumetric pipets.

6. Class A, 5 mℓ volumetric pipets.

7. Class A, 10 mℓ volumetric pipets.

8. Class A, 20 mℓ volumetric pipets.

9. Class A, 25 mℓ volumetric pipets.

10. Class A, 50 mℓ volumetric pipets.

11. Class A, 100 mℓ volumetric pipets.

12. Class A, 100 mℓ volumetric flasks.

13. Class A, 1000 mℓ Volumetric flasks.

14. Class A, 2000 mℓ volumetric flasks.

15. Mohr pipet, 1 mℓ graduated 1/10.

LIST OF REAGENTS

A list of reagents used in determination of SO_2 is provided indicating purity, manufacturer and catalog number. The function of each reagent in the procedure is also given.

1. Water - deionized and filtered through 0.22 micron filter.

2. Primary standard - Sulfuric acid, H_2SO_4, certified 0.1 N, formula weight = 98.08, ACS reagent grade, Fisher Scientific Company #SO-A-212.

3. Absorbant - Stabilized 30 percent hydrogen peroxide, H_2O_2, formula weight = 34.01, analytical reagent grade, Mallinckrodt #5239.

4. Eluent - Sodium bicarbonate, $NaHCO_3$, formula weight = 84.01, ACS analytical reagent grade powder, Mallinckrodt #7412.

5. Eluent - Sodium carbonate, Na_2CO_3, formula weight = 105.99, ACS analytical reagent grade anyhdrous power, Mallinckrodt #7521.

6. Regenerant - Sulfuric acid, H_2SO_4, formula weight = 98.08, ACS analytical reagent grade, Mallinckrodt #2876.

PREPARATION OF REAGENTS

Water is prepared by filtering deionized water through a 0.22 micron Millipore filter and storing in polyethylene bottles. All solutions and dilutions are made up to volume with water prepared in the above manner.

Primary Standard

The stock solution is prepared by diluting 20 mℓ of certified 0.1 N H_2SO_4 (4800 $\frac{\mu g\ SO_4^{-2}}{m\ell}$ to 1000 mℓ with water. The resulting solution contains

$96.0 \ \frac{\mu g \ SO_4^{-2}}{m\ell}$. More dilute standards are prepared by pipetting 0.5, 1, 1.5, 2, 3, 4, 8, 10, 20, 30, 40, 50, 60, 70, 80, and 90 mℓ of the stock solution into 100 mℓ volumetric flasks and making up the volume. These standards remain stable for at least fourteen weeks. All glassware used in the preparation of standards should be washed with 1:1 (v:v) nitric acid and then rinsed copiously with tap water with a final rinse of filtered deionized water.

Absorbing Solition (3 percent H_2O_2)

100 mℓ of 30 percent H_2O_2 is diluted to 1 liter with water.

Eluent (0.003 M $NaHCO_3$ + 0.0024 M Na_2CO_3)

Concentrated stock solutions of sodium bicarbonate and sodium carbonate are prepared in the following manner. For a 0.6 M solution of sodium bicarbonate, 50.41 g of solid sodium bicarbonate is dissolved in 1000 mℓ of water. For a 0.48 M solution of sodium carbonate, 50.88 g of solid sodium carbonate is dissolved in 1000 mℓ of water. The carbonate solution used as the eluent is made up by pipetting 10 mℓ of each stock solution into a 2 liter volumetric flask and diluting to mark with water.

Regenerate (1 N H_2SO_4)*

56 mℓ of 95 percent H_2SO_4 i[illegible] diluted to 2 liters with water.

*A total of 4 liters [illegible] these solutions are prepared to fill the 4 liter reservoirs in t[illegible]graph.

REFERENCES

Braker, W. and Mossman, A.L., Matheson Gas Data Book, 5th Edition, East Rutherford, N.J., 1971, pg. 513.

West, P.W. and Gaeke, G.C., Anal. Chem., Vol. 28, pg. 1816, 1956.

Adams, D.F., Corn, M., Harding, C.I., Pate, J.P., Plumley, A.L., Scaringelli, F.P., and Urone, P., "Methods of Air Sampling and Analysis," [Tentative Method of Analysis for Sulfur Dioxide Content of the Atmosphere (colormetric), No. 42401-01-69T], pg. 447, Amer. Pub. Health Ass., Washington, D.C., 1972.

"ASTM Standards - Water, Atmospheric Analysis," ASTM Designation D291470T, Part 23, Am. Soc. Test. Mat., Philadelphia, PA., 1972.

US EPA, Fed. Register, Vol. 36, No. 158, 15492, 1971.

Robinson, E. and Robbins, R.C., "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants," Final Report, SRI Project 6755 Supplement, Stanford Research Inst., Palo Alto, Calif., 1968.

Stern, A.C. (Ed.), Air Pollution, 3rd Edition, Academic Press, Inc., N.Y., 1976, Vol. 3, Pg. 214.

Zurlo, N. and Griffini, A.M., Med. Lav., Vol. 53, pg. 330, 1962.

Scaringelli, F.P., Elfers, L., Norris, D., and Hochheiser, S. Anal. Chem., Vol. 42, pg. 1818, 1970.

Pate, J.B., Ammons, B.E., Swanson, G.A., Lodge, Jr., J.P., Anal. Chem., Vol. 37, pg. 942, 1965.

Pate, J.B., Lodge, Jr., J.P., and Wartburg, A.F., Anal. Chem., Vol. 34, pg. 1660, 1962.

Scaringelli, F.P., Saltzman, B.E., and Frey, S.A., Anal. Chem., Vol. 39, pg. 1709, 1967.

Stern, A.C. (Ed.), Air Pollution, 3rd Edition, Academic Press, Inc., N.Y. 1976, Vol. 3, pg. 214

Urone, P., Evans, J.B., and Noyes, C.H., Anal. Chem., Vol. 37, pg. 1104, 1965.

Bostrom, C.E. Int. J. Air Water Poll., Vol. 9, pg. 333, 1965.

Attari, A., Igielski, R.P., and Jaselskis, B., Anal. Chem, Vol. 42, pg. 1282, 1970.

Kawai, T., Netsu Kanri, Vol. 22, pg. 20, 1970.

Thomas, M.D., Ivie, J.O., and Fitt, T.C., Ind. Eng. Chem., Anal, Ed., Vol. 18, pg. 383, 1946.

Yocum, J.E., Richardson, R.L., Saslaw, I.M., and Chapman, S., Proc. 49th Ann. Meet. Air Poll. Contr., Ass., Pittsburgh, Pa., 1956.

Kuczynski, E.R., Environm. Sci. Tech., Vol. 1, pg. 68, 1967.

Shikiya, J.M. and McPhee, R.D., 61st Annual Meeting, Paper No. 68-72, Air Poll. Conr. Ass., Pittsburgh, Pa., 1968.

Jacobs, M.B., The Chemical Analysis of Air Pollutants, Chapter 8, Wiley (Interscience), New York, N.Y., 1960.

Jacobs, M.B., The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents, Chapter 9, Wiley (Interscience), New York, N.Y., 1949.

Katz, M., Anal. Chem., Vol. 22, pg. 1040, 1950.

Stratman, H., Mikrochim, Acta. Vol. 6, pg. 688, 1954.

Pate, J.B., Lodge, Jr., J.P., and Neary, M.P., Anal. Chem. Acta., Vol. 28, pg. 341, 1963.

Lodge, Jr., J.P., Pate, J.B., and Huitt, H.A., Amer. Ind. Hyg. Ass., J., Vol. 24, pg. 380, 1963.

Forrest, J. and Newman, L., Atmos. Environ. Vol. 7, pg. 561, 1973.

Huygen, C., Anal. Chim, Acta. Vol. 28, pg. 349, 1963.

Harding, J., and Schlein, B., "Nuclear Techniques in Environmental Pollution," SM-142a/9, IAEA, Vienna, Austria, 1971.

Wilsdon, B.H. and McConnell, F.J., J. Soc. Chem. Ind. Vol. 53, pg. 385, 1934.

Huey N.A., J. Air Poll. Cont. Ass., Vol. 18, pg. 610, 1968.

Thomas, F.W. and Davidson, C.M., J. Air Poll. Cont. Ass., Vol. 11, pg. 1. 1961.

Stalker, W.W., Dickerson, R.C., and Kramer, G.D., Amer. Ind. Hyg. Ass., J., Vol. 24, pg. 68, 1963.

Hickey, H.R. and Hendrickson, E.R., J. Air Poll. Cont. Ass., Vol. 15, pg. 409, 1965.

Harding, C.I., and Kelley, T.R., J. Air Poll. Cont. Ass., Vol. 17, pg. 545, 1967.

Stevens, R.K., Mulik, J.D., O'Keeffe, A.E., and Krost, K.J., Anal. Chem., Vol. 43, pg. 827, 1971.

Stevens, R.K., O'Keefe, A.E., and Ortman, G.C., Environ. Sci, Tech., Vol. 3, og. 652, 1969.

Ronkainen, P., Denslow, J., Leppanen, O., J. Chromatog. Sci,, Vol. 11, pg. 384, 1973.

Pescar, R.E., and Hartman, C.H., J. Chromatog. Sci., Vol. 11, pg. 492, 1973.

Stevens, R.K., and O'Keefe, A.E., Anal. Chem., Vol. 42, pg. 143a, 1970.

Bruner, F., Liberti, A., Possanzini, M., and Allegrini, I., Anal. Chem., Vol. 44, pg. 2070, 1972.

Bruner, F., Ciccioli, P., and DiNardo, F., Anal. Chem., Vol. 47, pg. 141, 1975.

Bruner, F., Ciccioli, P., and DiNardo, F., J. Chromatog. Vol. 99, pg. 661, 1974.

Bremner, J.M., and Banwart, W.L., Sulfur Inst. Journal, Vol. 10, pg. 6, 1974.

Mulik, J.D., Todd, G., Estes, E., and Sawicki, E., "Ion Chromatography Determination of Atmospheric Sulfur Dioxide," Symposium on Ion Chromatographic Analysis of Environmental Pollutants, EPA, Research Triangle Park, N.C., April, 1977.

Dietzmann, H.E., "Protocol to Characterize Gaseous Emissions as a Function of Fuel and Additive Composition," Environmental Protection Technology Series under Contract 68-02-1275, September, 1975.

DeSouza, T.L.C., Lane, D.C., and Bhatia, S.P., Anal. Chem., Vol. 47, pg. 543, 1975.

APPENDIX F

NITROUS OXIDE PROCEDURES

THE MEASUREMENT OF NITROUS OXIDE IN EXHAUST

This procedure was developed to measure nitrous oxide (N_2O) in dilute gasoline and diesel exhaust. Standard CVS bag samples are analyzed for N_2O using calibration blends to quantify the results. Gas chromatograph peak areas are obtained using a Hewlett-Packard 3354 computer system. This technique has a minimum detection limit of less than 0.01 ppm. The total system schematic for the analysis of N_2O in exhaust is shown in Figure 1.

ANALYTICAL SYSTEM

The analysis for N_2O in exhaust is conducted with a gas chromatograph system using a Perkin-Elmer Model 3920B electron capture detector. The system employs two pneumatically operated electrically controlled Seiscor valves, an analytical column, and a stripper column. The gas chromatograph separation is obtained at room temperature. A special control console was fabricated to house the entire system except for the electron capture detector.

A stripper column is included as a precautionary measure to prevent unwanted heavier molecular weight exhaust species from entering the analytical system. Figure 2 (Step 1) illustrates the gas chromatograph flow schematic with the gas sampling valve in the purge position and the backflush valve is foreflushing to the analytical column. Figure 3 (Step 2) illustrates the flow schematic when the gas sampling valve is actuated and the backflush valve still in the foreflush position to the analytical column. Once the N_2O peak foreflushing has eluted, the backflush valve is activated and the heavier molecular weight species retained on the stripper column are backflushed to vent, as shown in Figure 4. A summary of the individual steps is presented below:

	Gas Sampling Valve		Backflush Valve	
Step	Position	Function	Position	Function
1	off	purge GSV w/sample	off	foreflush to analytical column
2	on	sample injected	off	foreflush to analytical column
3	on	sample injected	on	backflush to vent

Under normal conditions, it is not necessary to backflush the calibration standards since they are free of contaminants that would interfere with

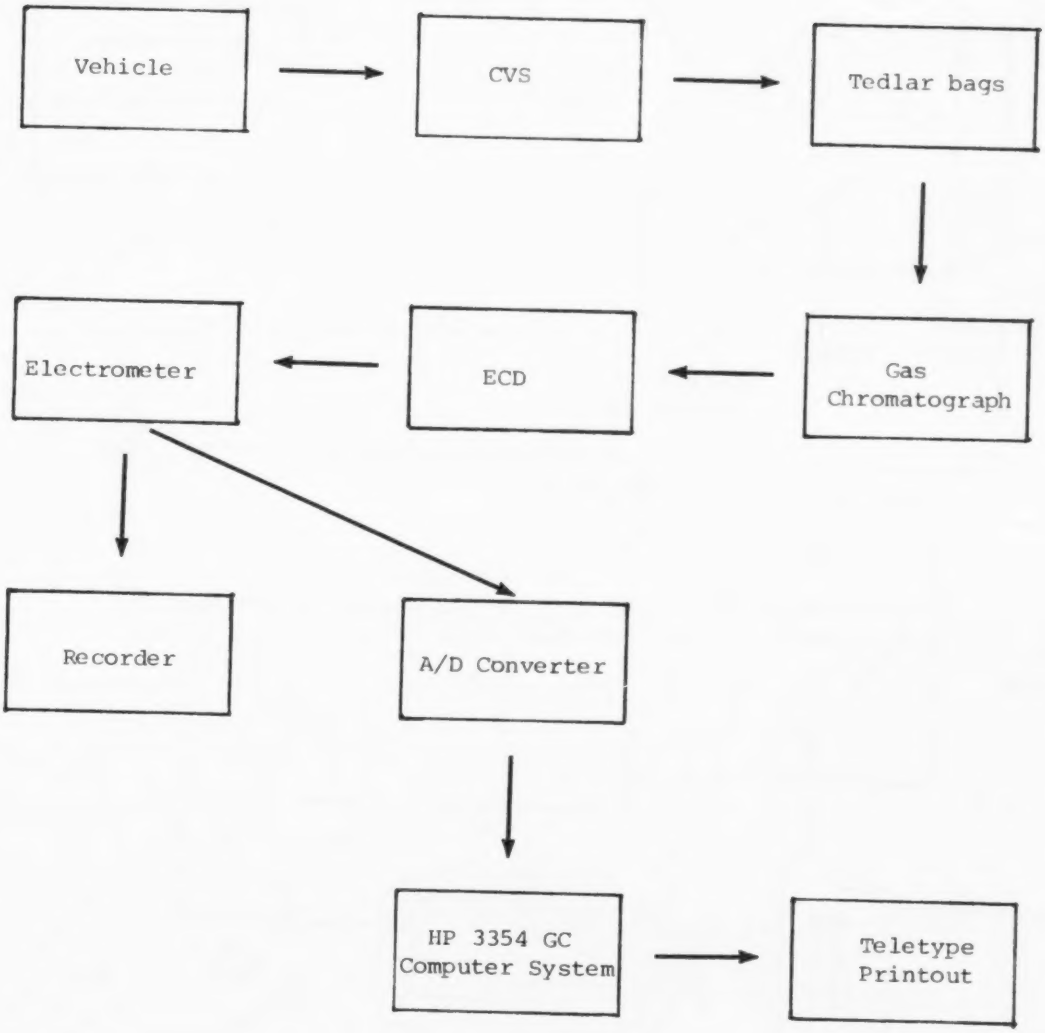

Vehicle
CVS
Tedlar bags
Gas Chromatograph
ECD
Electrometer
Recorder
A/D Converter
HP 3354 GC Computer System
Teletype Printout

Figure 1. Total system flow schematic for the analysis of nitrous oxide in exhaust.

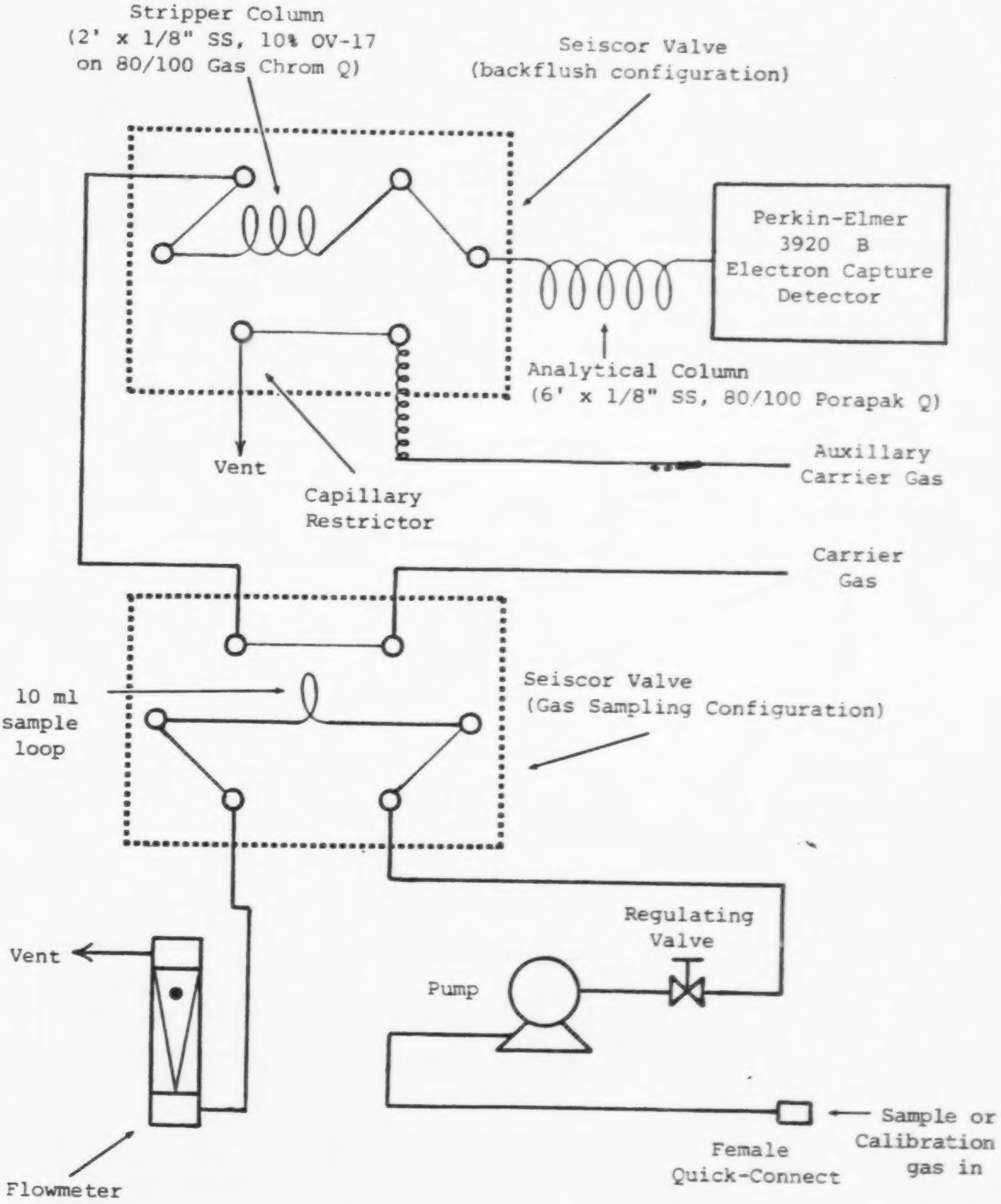

Stripper Column
(2' x 1/8" SS, 10% OV-17
on 80/100 Gas Chrom Q)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920 B
Electron Capture
Detector
Analytical Column
(6' x 1/8" SS, 80/100 Porapak Q)
Auxillary
Carrier Gas
Vent
Capillary
Restrictor
Carrier
Gas
10 ml
sample
loop
Seiscor Valve
(Gas Sampling Configuration)
Regulating
Valve
Vent
Pump
Sample or
Calibration
gas in
Female
Quick-Connect
Flowmeter

Figure 2. Flow schematic of nitrous oxide analytical system (Step 1 - Purge of sample loop of GSV).

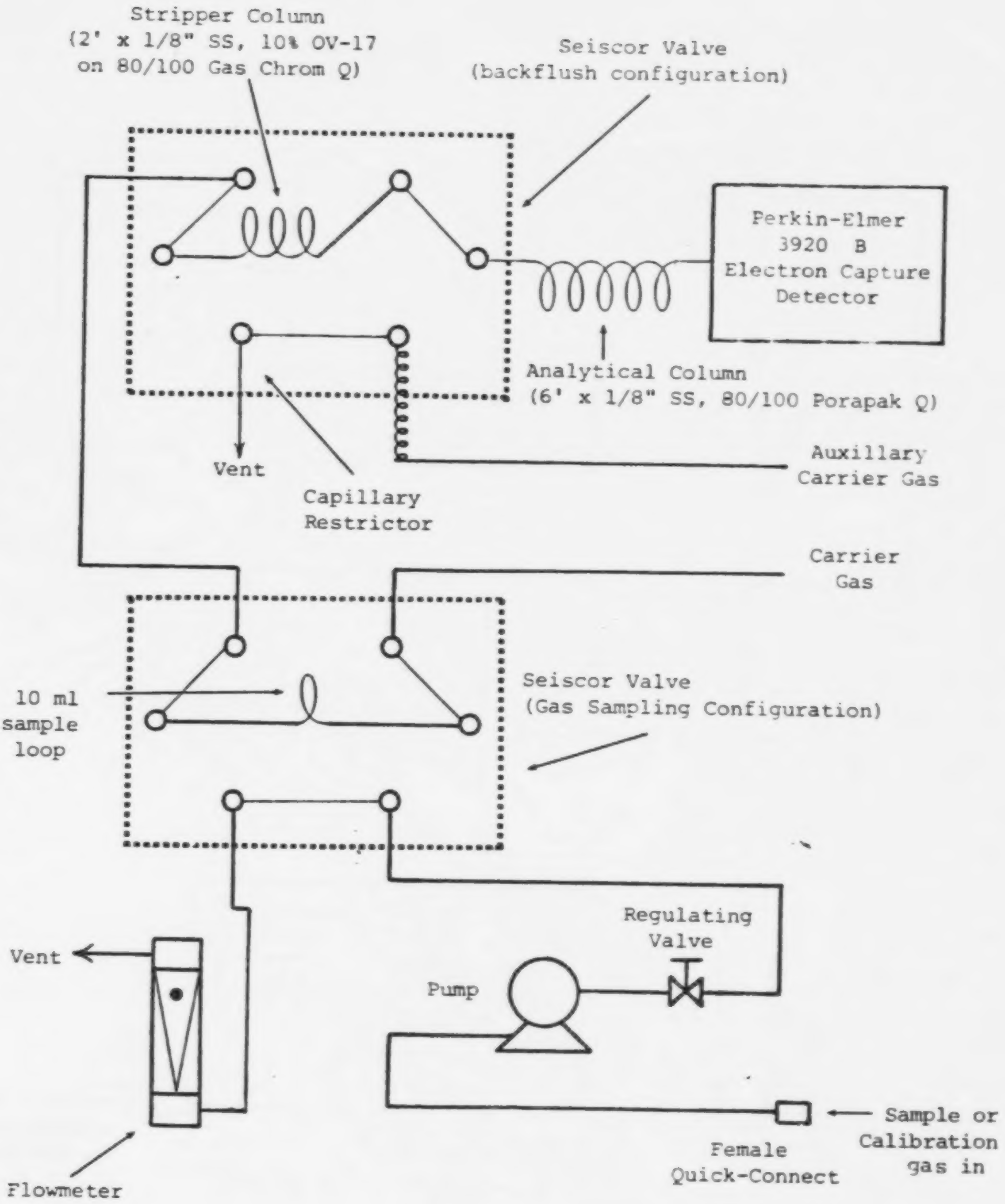

Stripper Column
(2' x 1/8" SS, 10% OV-17
on 80/100 Gas Chrom Q)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920 B
Electron Capture
Detector
Analytical Column
(6' x 1/8" SS, 80/100 Porapak Q)
Vent
Capillary
Restrictor
Auxillary
Carrier Gas
Carrier
Gas
10 ml
sample
loop
Seiscor Valve
(Gas Sampling Configuration)
Regulating
Valve
Vent
Pump
Sample or
Calibration
gas in
Female
Quick-Connect
Flowmeter

Figure 3. Flow schematic of nitrous oxide analytical system (Step 2 - Inject sample or calibration gas into system).

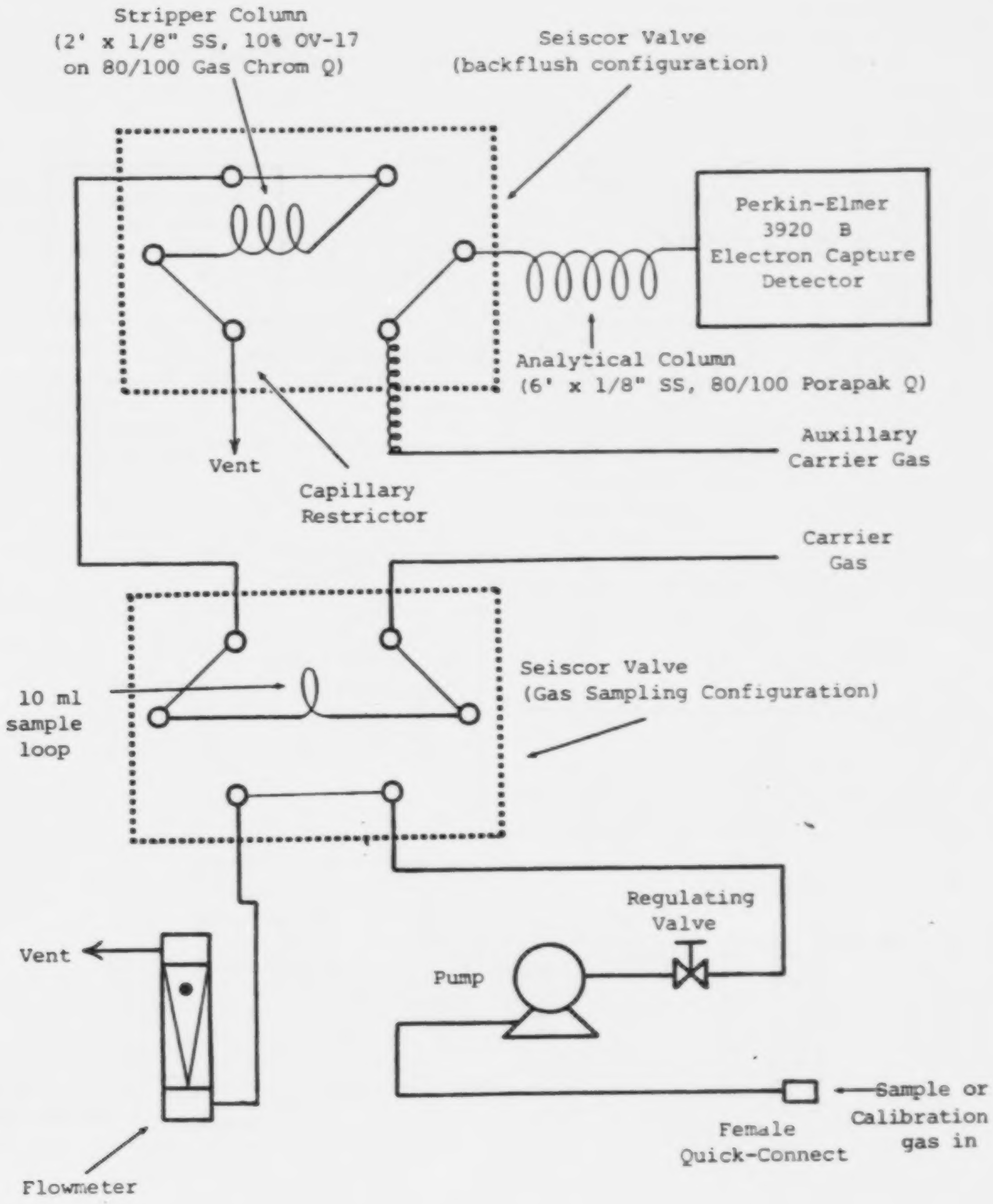

Stripper Column
(2' x 1/8" SS, 10% OV-17
on 80/100 Gas Chrom Q)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920 B
Electron Capture
Detector
Analytical Column
(6' x 1/8" SS, 80/100 Porapak Q)
Auxillary
Carrier Gas
Vent
Capillary
Restrictor
Carrier
Gas
Seiscor Valve
(Gas Sampling Configuration)
10 ml
sample
loop
Regulating
Valve
Vent
Pump
Sample or
Calibration
gas in
Female
Quick-Connect
Flowmeter

Figure 4. Flow schematic of nitrous oxide analysis system (Step 3 - Backflush OV-17 stripper column).

the analytical column. A typical gas chromatograph trace for a calibration blend is shown in Figure 5. A baseline separation is obtained and the N_2O peak area is obtained using a Hewlett-Packard 3354 GC computer system.

On gasoline and diesel samples it is necessary that the backflush is inlcuded in the analysis to prevent contamination of the analytical column. Using the system described, 60 seconds are allocated to the foreflush position and 360 seconds are allowed for backflushing the stripper column. A typical gasoline-CVS sample GC trace along with the gas chromatograph operating conditions is presented in Figure 6.

CONTROL SYSTEM

The control of the two Seiscor valves if accomplished by ATC timers and ASCO electric solenoid valves. The electrical schematic for the control of the Seiscor valves using these timers and electric solenoid valves is shown in Figure 7. The flow schematic for vacuum and pressure lines to the Seiscor valve are presented in Figures 8-10.

SAMPLE CALCULATIONS

The quantification of N_2O in exhaust is based on a direct comparison of the N_2O in exhaust with a calibration blend of a known N_2O concentration. Two basic assumptions are made in these calculations that should be considered with other systems. The first assumption is that the electron capture detector has a linearized output and that measurements are made within the working range of the system. These two parameters were verified for this procedure using instruments previously described. Working within the linear range of a given gas chromatograph equipped with an electron capture detector, the following relationship is true.

Let Csam = ppm concentration of N_2O in sample

Cstd = ppm cpncentration of N_2O in standard

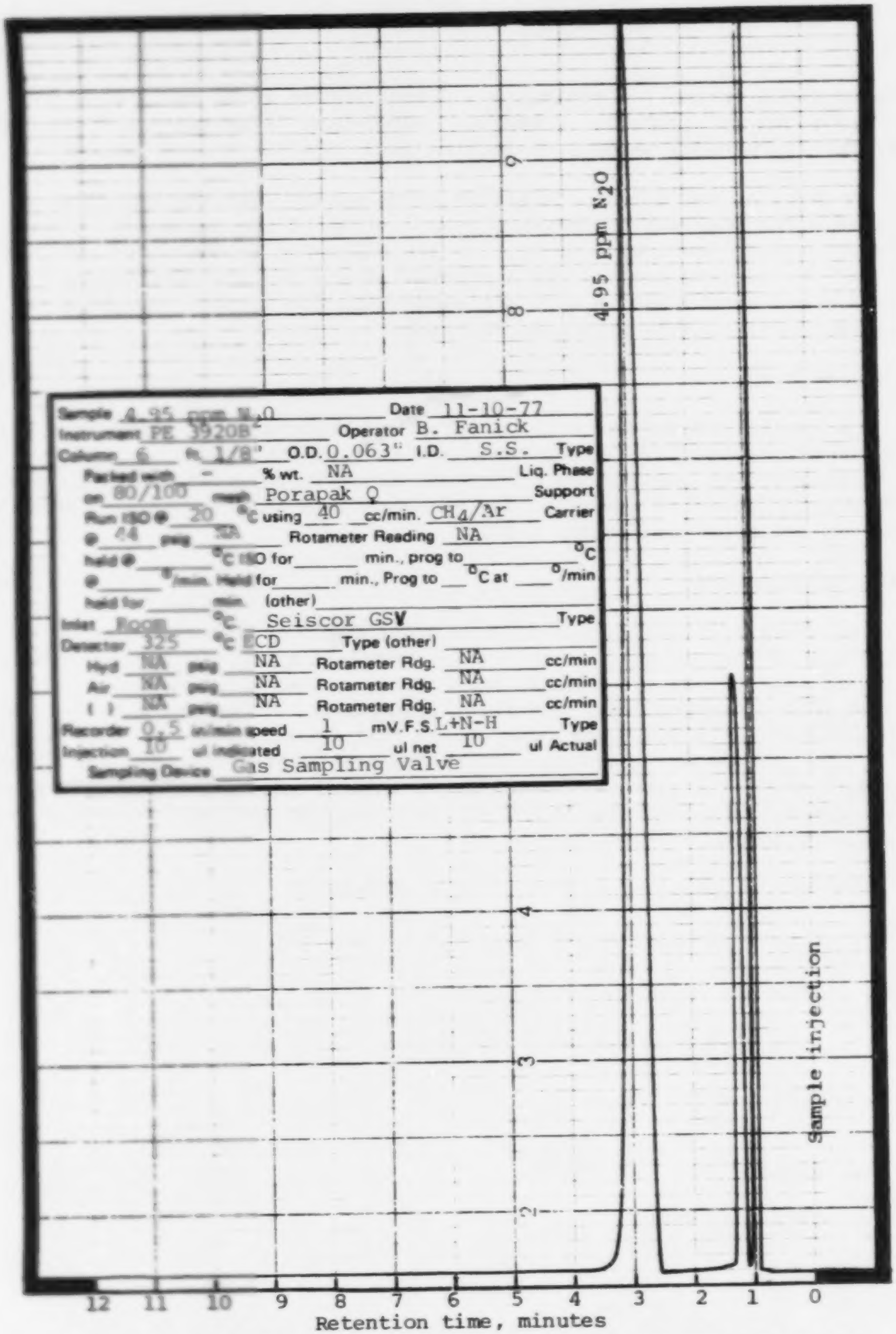
Asam = area of N_2O peak in sample

Astd = area of N_2O peak in standard

$$\frac{Astd}{Cstd} = \frac{Asam}{Csam}$$

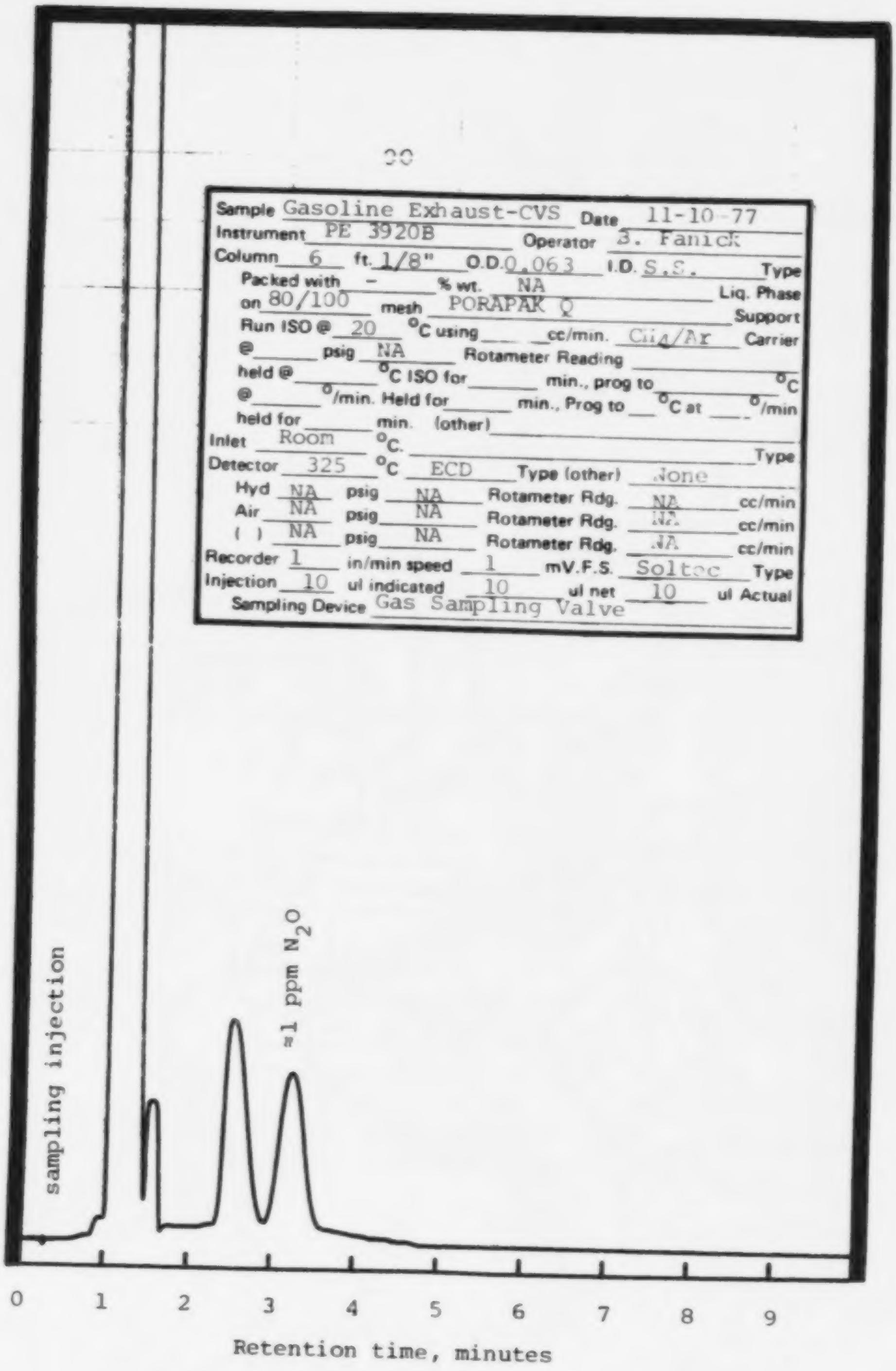
Solving for Csam

$$Csam = \frac{Asam \times Cstd}{Astd}$$



Sample 4.95 ppm N_2O Date 11-10-77
Instrument PE 3920B Operator B. Fanick
Column 6 ft. 1/8" O.D. 0.063" I.D. S.S. Type
Packed with - % wt. NA Liq. Phase
on 80/100 mesh Porapak Q Support
Run ISO @ 20 °C using 40 cc/min. CH_4/Ar Carrier
@ 44 psig NA Rotameter Reading NA
held @ °C ISO for min., prog to °C
@ °/min. Held for min., Prog to °C at °/min
held for min. (other)
Inlet Room °C Seiscor GSV Type
Detector 325 °C ECD Type (other)
Hyd NA psig NA Rotameter Rdg. NA cc/min
Air NA psig NA Rotameter Rdg. NA cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 0.5 in/min speed 1 mV.F.S. L+N-H Type
Injection 10 ul indicated 10 ul net 10 ul Actual
Sampling Device Gas Sampling Valve

Figure 5. Typical N_2O calibration blend gas chromatograph trace.



Sample Gasoline Exhaust-CVS Date 11-10-77
Instrument PE 3920B Operator 3. Fanick
Column 6 ft. 1/8" O.D. 0.063 I.D. S.S. Type
Packed with – % wt. NA Liq. Phase
on 80/100 mesh PORAPAK Q Support
Run ISO @ 20 °C using ___ cc/min. CH_4/Ar Carrier
@ ___ psig NA Rotameter Reading ___
held @ ___ °C ISO for ___ min., prog to ___ °C
@ ___ °/min. Held for ___ min., Prog to ___ °C at ___ °/min
held for ___ min. (other) ___
Inlet Room °C. ___ Type
Detector 325 °C ECD Type (other) None
Hyd NA psig NA Rotameter Rdg. NA cc/min
Air NA psig NA Rotameter Rdg. NA cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 in/min speed 1 mV.F.S. Soltec Type
Injection 10 ul indicated 10 ul net 10 ul Actual
Sampling Device Gas Sampling Valve

Figure 6. Typical gasoline-CVS exhaust sample.

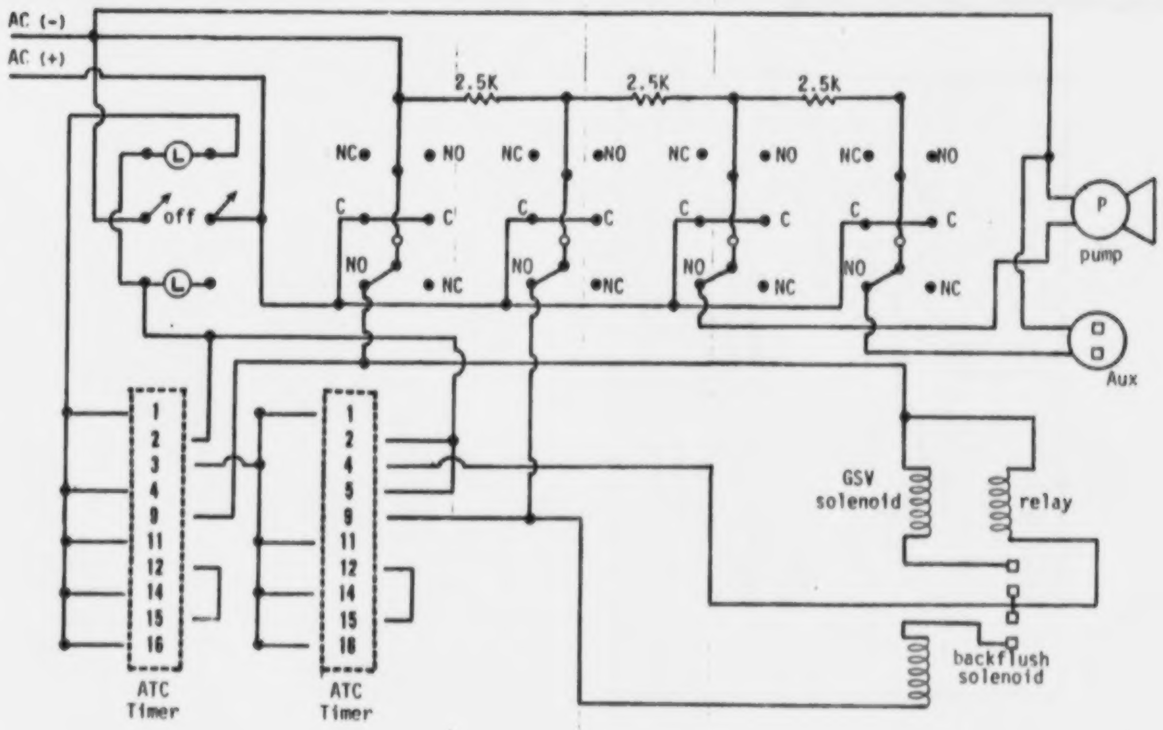
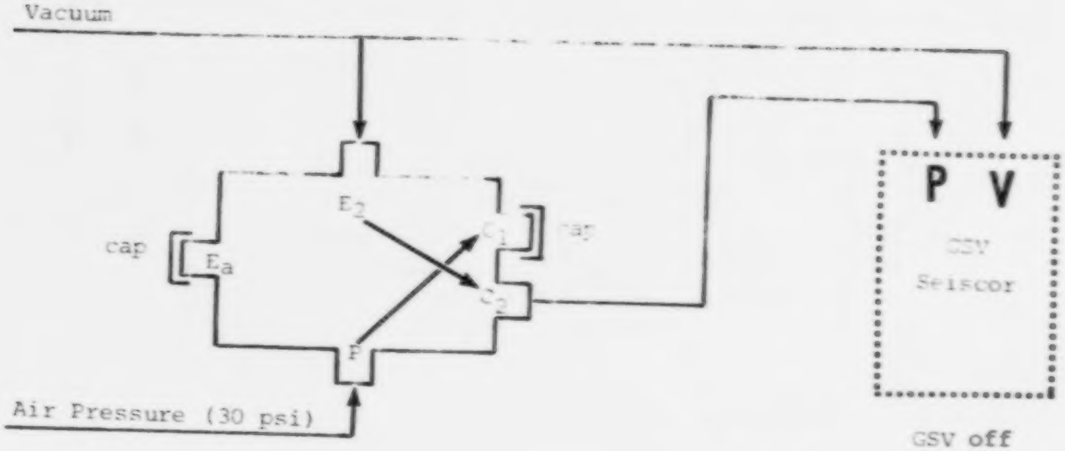
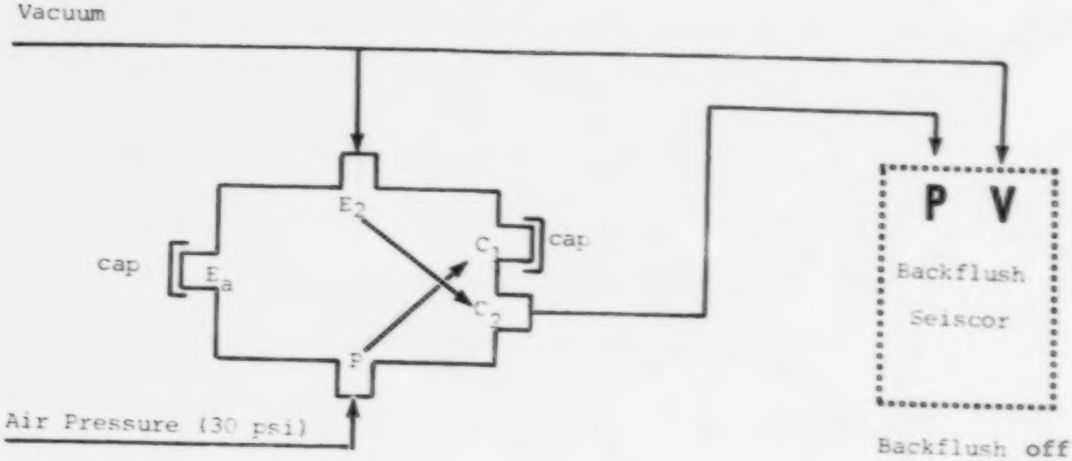

AC (-)
AC (+)
off
2.5K
2.5K
2.5k
NC
NO
C
NC
NO
C
NC
NO
C
NC
NO
C
NO
NC
NO
NC
NO
NC
NO
NC
P
pump
Aux
GSV solenoid
relay
backflush solenoid
1
2
3
4
9
11
12
14
15
16
ATC Timer
1
2
4
5
9
11
12
14
15
16
ATC Timer

Figure 7. Electrical schematic for nitrous oxide analysis system.


Vacuum
E2
cap
Ea
C1
cap
C2
P
Air Pressure (30 psi)
P V
GSV
Seiscor

GSV off


Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
Backflush
Seiscor

Backflush off

Figure 8. Flow schematic in electric solenoid valves (Both valves de-energized).

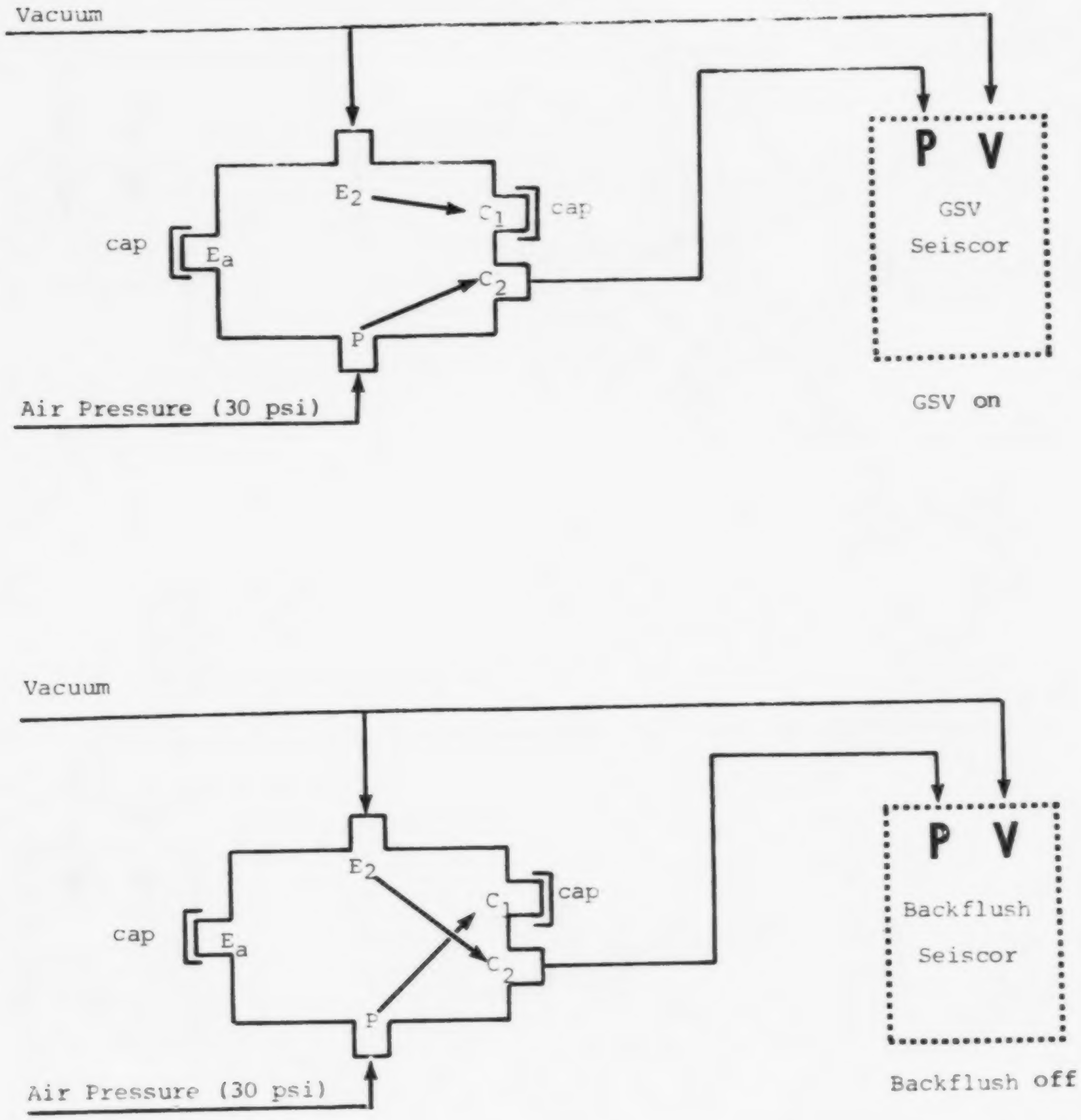
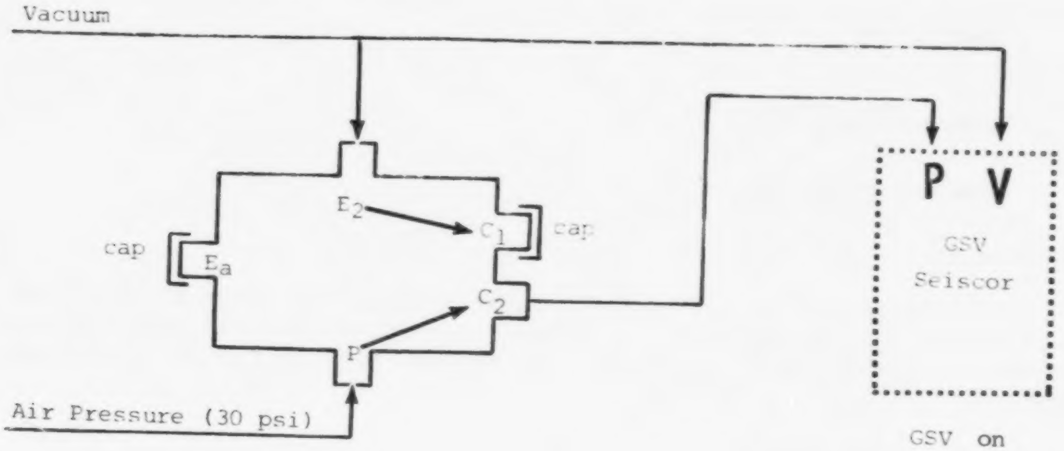
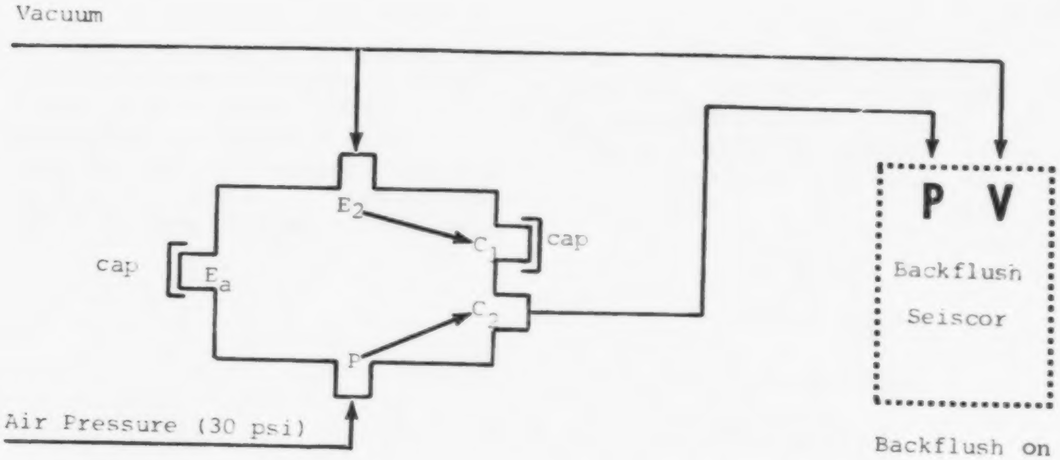

Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
GSV
Seiscor
GSV on
Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
Backflush
Seiscor
Backflush off

Figure 9. Flow schematic in electric solenoid valves (GSV energized, backflush de-energized).


Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
GSV
Seiscor

GSV on


Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
Backflush
Seiscor

Backflush on

Figure 10. Flow schematic in electric solenoid valves (Both valves energized).

Example 1:

A 4.95 ppm N_2O (in nitrogen) calibration blend was found to give 5291 area counts for the N_2O peak. An exhaust sample was found to give 2674 area counts for the N_2O peak. Calculate the N_2O in the exhaust sample.

$$Csam = \frac{Asam \times Cstd}{Astd}$$

$$Csam = \frac{2674 \times 4.95}{5291}$$

$$Csam = 2.50 \text{ ppm } N_2O$$

Example 2:

A 1.13 ppm N_2O (in nitrogen) calibration blend was found to give 1208 area counts for the N_2O peak. An exhaust sample was found to give 534 area counts for the N_2O peak. Calculate the concentration of N_2O in the exhaust sample.

$$Csam = \frac{Asam \times Cstd}{Astd}$$

$$Csam = \frac{534 \times 1.13}{1208}$$

$$Csam = 0.50 \text{ ppm } N_2O$$

EQUIPMENT

This analysis is performed using a gas chromatograph equipped with an electron capture detector. The detector, detector heater controls, electrometer, recorder and GC integrator are major electronic components in the detection system. A control console was fabricated to house the mechanical hardware items that are necessary for the proper operation of the N_2O analysis system. Figure 11 illustrates the complete analytical system for measuring N_2O in exhaust. The major items that are included in each of these systems is listed below:

Gas Chromatograph

1. Perkin-Elmer Model 3920B gas chromatograph
2. Linerarized electron capture detector (ECD)
3. Leeds and Northrup Model W 1 mv recorder
4. Hewlett-Packard Model 3354 GC computer system

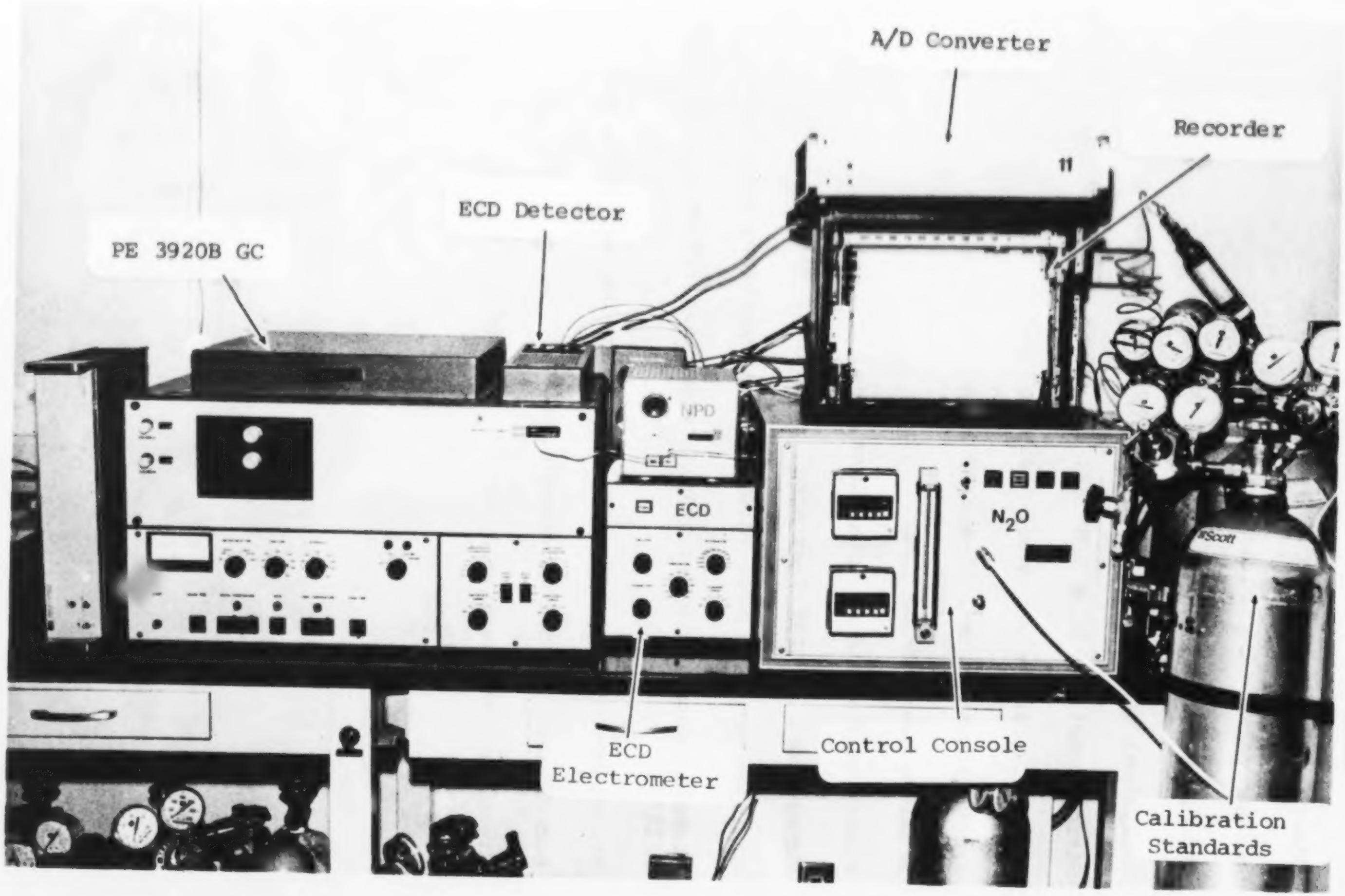

A/D Converter
Recorder
ECD Detector
PE 3920B GC
NPD
ECD
N_2O
ECD
Electrometer
Control Console
Calibration
Standards

Figure 11. Nitrous oxide analytical system.

5. Hewlett-Packard Model 1865A A/D Converter

Control Console System

1. Seiscor valve - gas sampling configuration
2. Seiscor valve - backflush configuration
3. ATC timers, Model 325A364A10PX (2 ea)
4. Analytical column, 6' x 1/8" SS, 120/150 Porapak Q
5. Stripper column, 2' x 1/8" SS, 10% OV-17 on 80/100 Gas Chrom Q
6. ASCO solenoid valve, Model 834501 (2 ea)
7. Brook flowmeter, R-2-15-A w/SS float, 0-150 scale
8. Metal Bellows MB-155 pump
9. Female quick-connect, stainless steel
10. Nupro Model 2M stainless steel regulating valve
11. Stainless steel tubing (0.01"ID) for capillary restrictor
12. Miscellaneous stainless steel, copper and Teflon tubing (1/8" and 1/16")
13. Miscellaneous stainless steel and brass unions, tees, etc.
14. Bud Classic II control console cabinet
15. Miscellaneous electrical on-off- switches

REFERENCES

Braker, W. and Mossman, A.L., Matheson Gas Data Book, 5th Edition, East Rutherford, N.J., 1971, pg. 431.

Jay, B. and Wilson, R., J. Appl. Phys., Vol. 15, No. 2, pg. 298, 1960.

De Grazio, R., J. Gas Chromatog., Vol. 3, pg. 204, 1965.

F & M Applications Chromatogram, 1942, F & M Scientific Division of Hewlett-Packard Corp., Avondale, Pa.

Porapak Brochure, Waters Associates, Framingham, Mass.

Bethea, R., and Adams, F., J. Chromatog., Vol. 10, pg. 1, 1963.

Leithe, W., The Analysis of Air Pollutants, Humphrey Sci. Pub., Ann Arbor, Michigan, 1970, pg. 176.

Private communication between Dr. R.B. Zweidinger and Frank Black of EPA and Harry Dietzmann of SwRI.

LaHue, M.D., Axelrod, H.D., and Lodge Jr., J.P., Anal. Chem., Vol. 43, pg. 1113, 1974.

APPENDIX G

HYDROGEN SULFIDE PROCEDURE

THE MEASUREMENT OF HYDROGEN SULFIDE IN EXHAUST

The measurement of hydrogen sulfide in dilute automotive exhaust is accomplished by bubbling dilute exhaust through glass impingers containing a buffered zinc acetate absorbing solution. The hydrogen sulfide reacts with the zinc acetate to form zinc sulfide which remains in solution. The exhaust sample is collected continuously during a test cycle. Upon completion of the test, the absorbing solution is treated with N,N dimethyl-para - phenylene diamine sulfate and ferric ammonium sulfate. This reaction produces a highly colored heterocyclic compound, methylene blue (3,9 - bis-dimethylaminophenazothionium sulfate). This colored solution is analyzed with a spectrophotometer at 667 nm in a 1 cm or 4 cm pathlength cell. The results are quantified by comparison to a standard curve. The minimum detectable concentration is 0.01 ppm.

SAMPLING SYSTEM

Two glass impingers in series, each containing 50 mℓ (10 mℓ buffered zinc acetate solution and 40 mℓ freshly vacuum boiled deionized water) of buffered zinc acetate absorbing solution, are used to collect exhaust samples for the analysis of hydrogen sulfide. A flow schematic of the sample collection system is shown in Figure 1. The two impingers together trap approximately 99+ percent of the hydrogen sulfide. The temperature of the impinger is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4 ℓ/minute by the sample pump. A dry gas meter is used to determine the total flow through the impinger during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allows continuous monitoring of the sample flow to insure proper flow rates during sampling. When sampling diesel fueled vehicles, a filter, located between the on-off solenoid valve and the dilution tunnel, is used to prevent diesel particulate from contaminating the sampling system. The lines connecting the filter to the dilution tunnel and the filter to the solenoid valve are heated to 175°F. Several views of the sampling system are shown in Figure 2.

DESCRIPTION OF METHOD

Hydrogen sulfide is collected in a buffered zinc acetate absorbing reagent from dilute automotive exhaust. The highly colored species, methylene blue, is generated by the addition of N,N dimethyl-para-phenylene diamine sulfate and ferric ion. Methylene blue has an absorbance maxima in the red region of the visible spectrum. The extinction wavelength curve for methylene blue is shown in Figure 3.

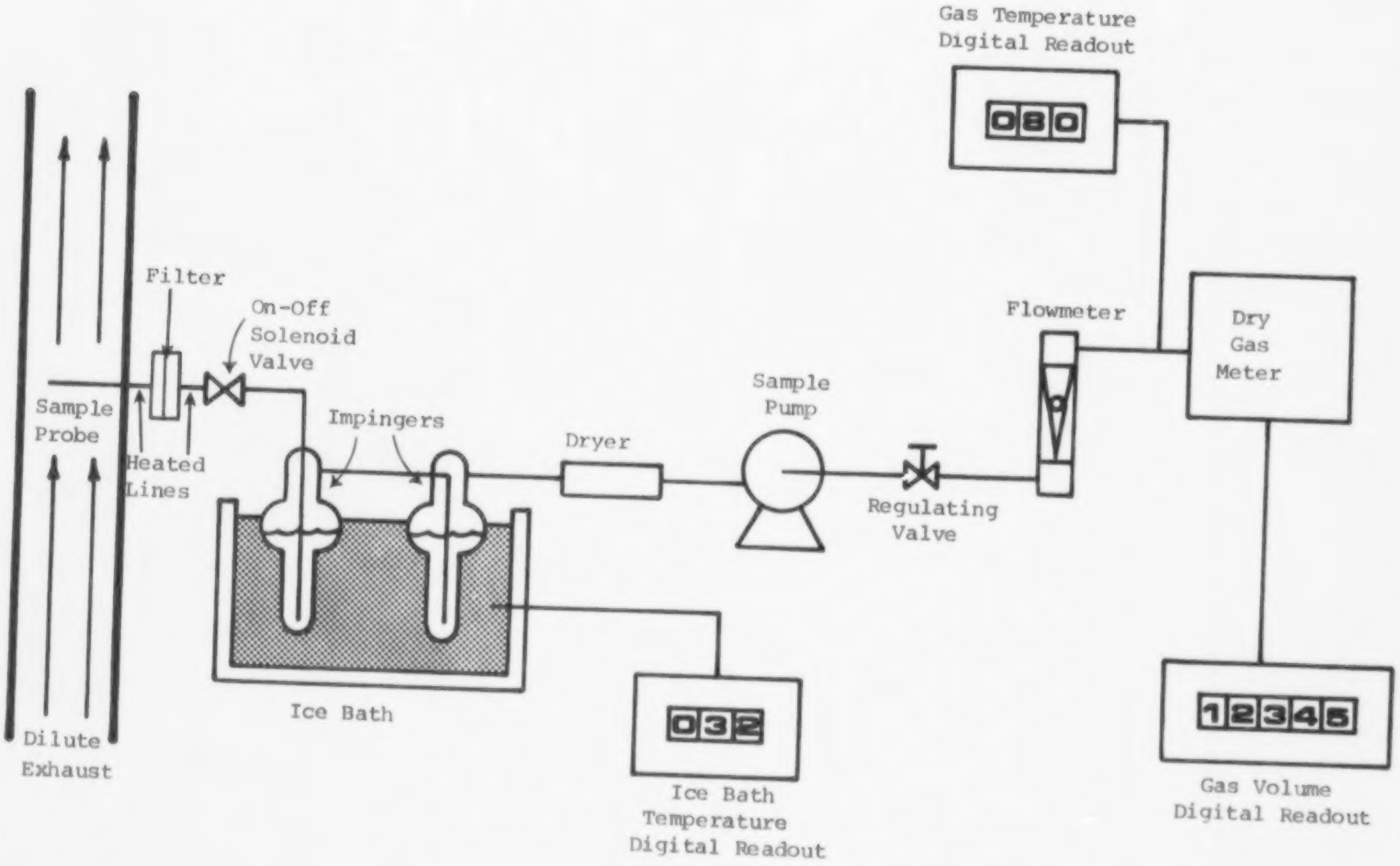
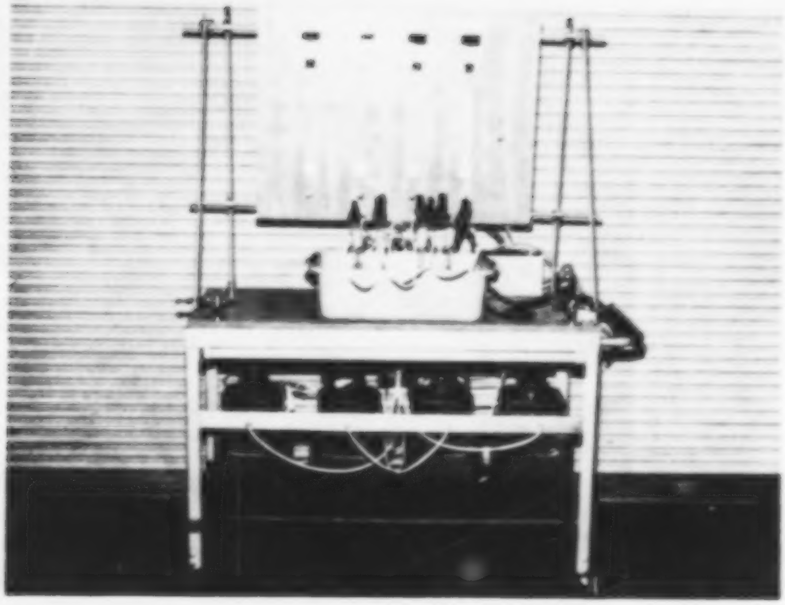
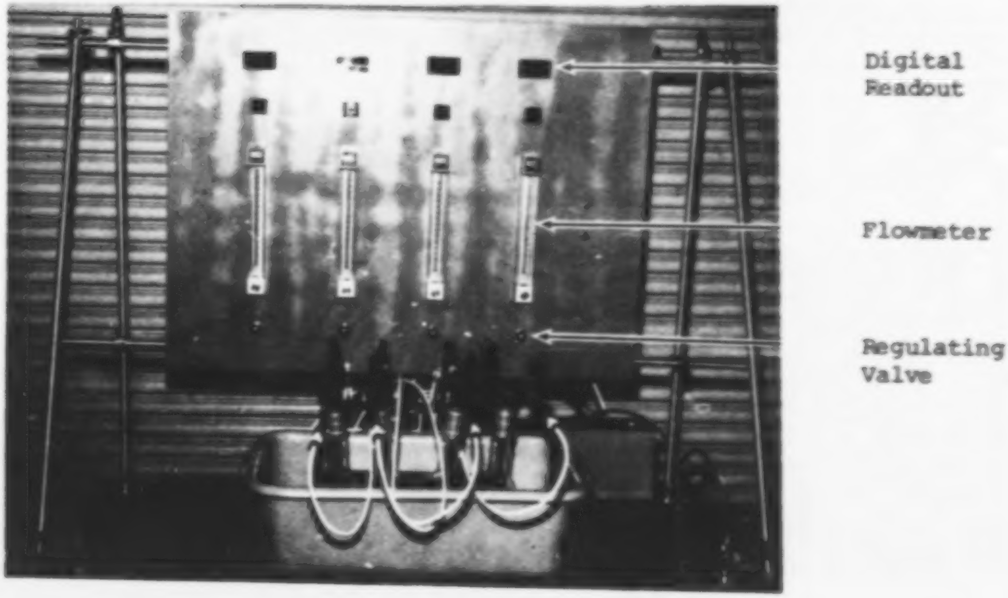

Gas Temperature
Digital Readout
080
Filter
On-Off
Solenoid
Valve
Flowmeter
Dry
Gas
Meter
Sample
Probe
Impingers
Sample
Pump
Dryer
Heated
Lines
Regulating
Valve
Ice Bath
Dilute
Exhaust
032
Ice Bath
Temperature
Digital Readout
12345
Gas Volume
Digital Readout

Figure 1. Hydrogen sulfide sample collection flow schematic.

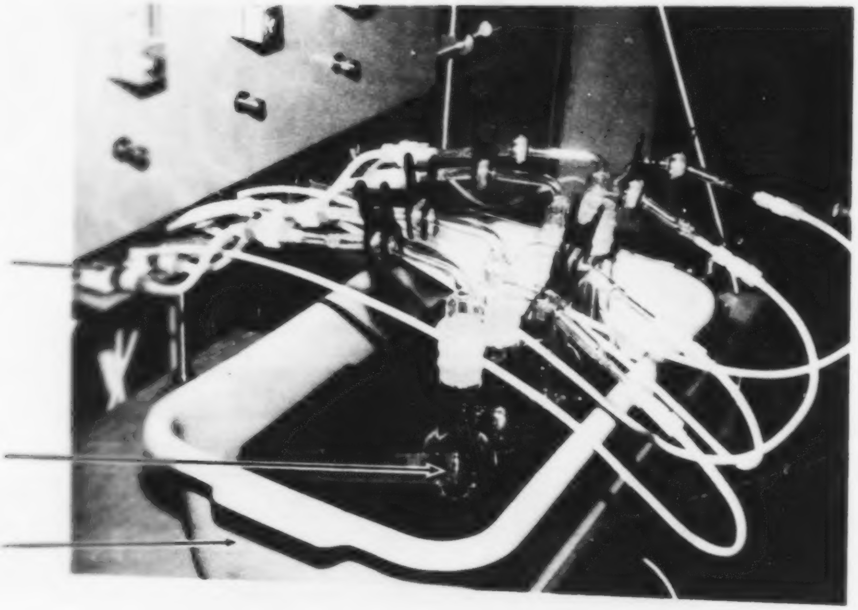


Front View

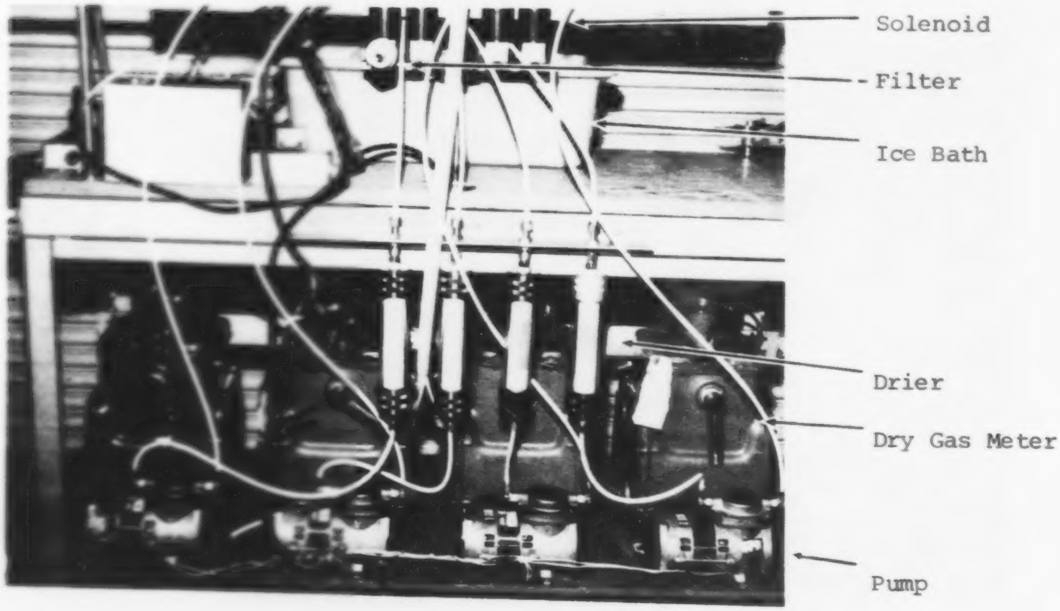

Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. The dilute exhaust sampling system for hydrogen sulfide.



Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). The dilute exhaust sampling system for hydrogen sulfide.

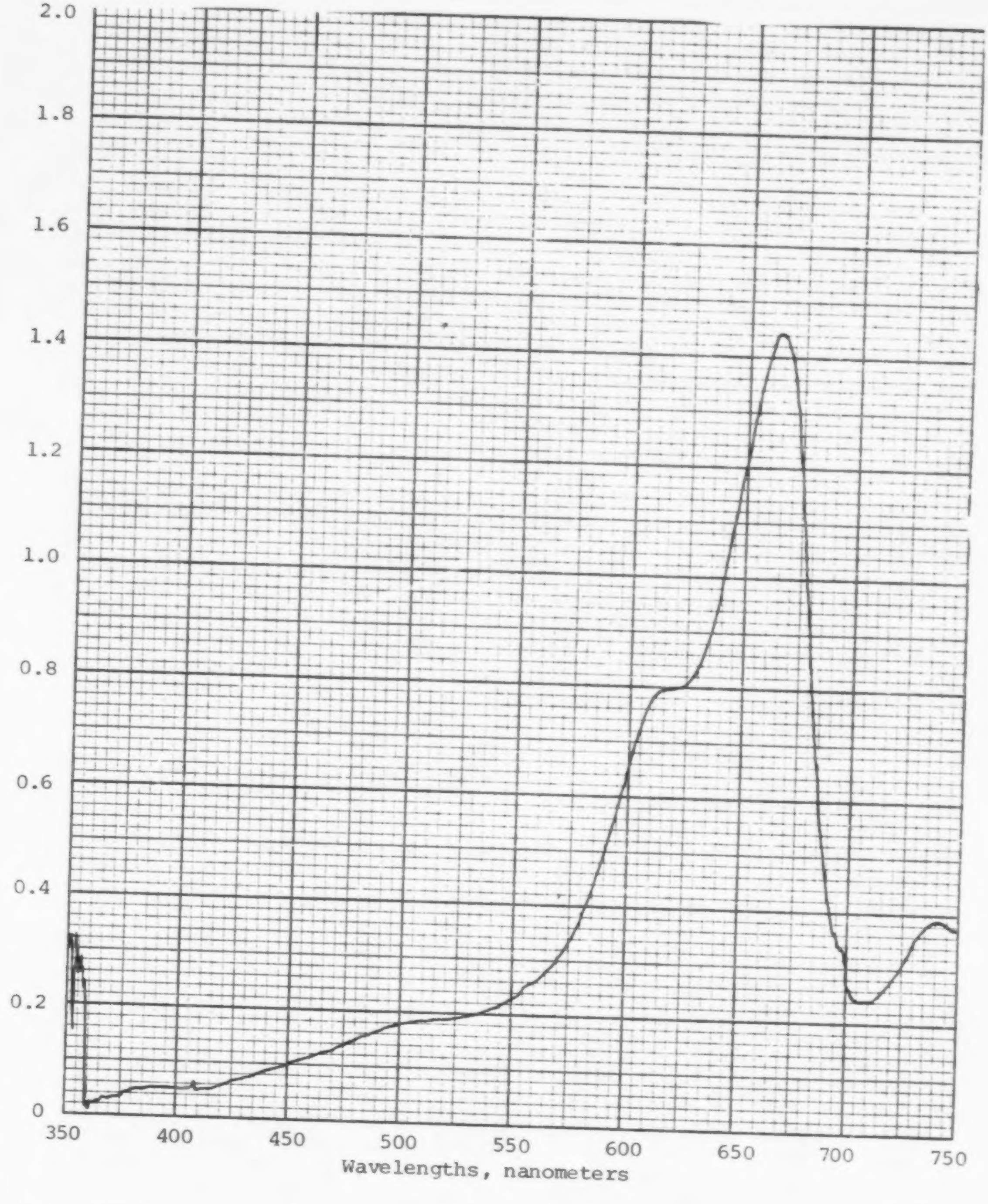


Figure 3. Extinction-wavelength curve of methylene blue.

The analytical procedure for the determination of hydrogen sulfide in dilute automotive exhaust consists of two major areas. The first is the standarization and calibration of the standard sulfide ion solution. The second area includes the sample acquisition and color development of the hydrogen sulfide sample. Each will be discussed in detail below. The analysis flow schematic for this procedure is shown in Figure 4.

Standardization and Calibration

The concentration of the standard sodium sulfide solution (approximately 0.03 M sodium sulfide in deionized water) is determined by an iodometric method. To three (3) Erlenmeyer flasks, 10 mℓ of the absorbing solution and 50 mℓ of the sulfide solution are added and the resulting solution is mixed. Into one of the flasks 5 mℓ of the 0.01 N iodine solution and 10 mℓ of concentrated hydrochloric acid are added. The resulting solution is immediately titrated to the starch endpoint with a standarized thiosulfate solution. This procedure is then repeated for the remaining two flasks and for two blanks prepared with only the absorbing reagent and 50 mℓ of vacuum boiled, deionized water. The excess iodine in the solution is reacted with the thiosulfate and the amount of sulfide ion present can be back-calculated.

The thiosulfate solution used to titrate the sulfide solution is standardized against primary standard grade potassium dichromate. The potassium dichromate is dreid in an oven at 150° to 200°C for 1 to 2 hours. A weighed 0.10 to 0.15 g (0.001 mole) portion of dried potassium dichromate is placed in a 500 mℓ Erlenmeyer flask and dissolved in 50 mℓ of deionized water. A freshly prepared solution of 3 g (0.02 mole) of potassium iodine, 5 mℓ of 6 N hydrochloric acid and 50 mℓ of deionized water is then added. This solution is gently swirled, covered with a watch glass, and allowed to stand for five (5) minutes. The sides of flask are then washed with deionized water followed by approximately 200 mℓ of deionized water. The resulting solution is titrated with the thiosulfate solution. As the end point is approached, about 5 mℓ of starch indicator is added. The solution is blue from the starch-iodine complex before the end point is reached. At the end point, there is a change in color from blue to green due to the production of Cr (III) ion. This standarized thiosulfate solution can then be used to standarize the dilute iodine solution as well as determine the sulfide ion concentration in the sulfide standard solution.

A concentrated iodine solution (~0.1 N) from which the dilute iodine solution is prepared is standarized against primary standard grade arsenic trioxide by an iodometric titration. A weighed portion of 0.15 to 0.20 g (0.001 mole) arsenic trioxide is placed into an Erlenmeyer flask. Then 10 to 20 mℓ of 1.0 M sodium hydroxide are added to dissolve the solid. With a small piece of blue litmus paper as the indicator, 1.0 M hydrochloric acid is added dropwise until the arsenic trioxide solution is slightly acidic. About 1.0 g (0.01 mole) of sodium bicarbonate is slowly added to prevent the loss of solution due to the effervescence of carbon dioxide. The resulting solution is diluted to about 100 mℓ. About 2 mℓ of the starch indicator is added and the solution is then titrated with the 0.1 N iodine solution. During the titration, the top of the buret should be covered to minimize the volatilization of iodine. The standarization needs to be done

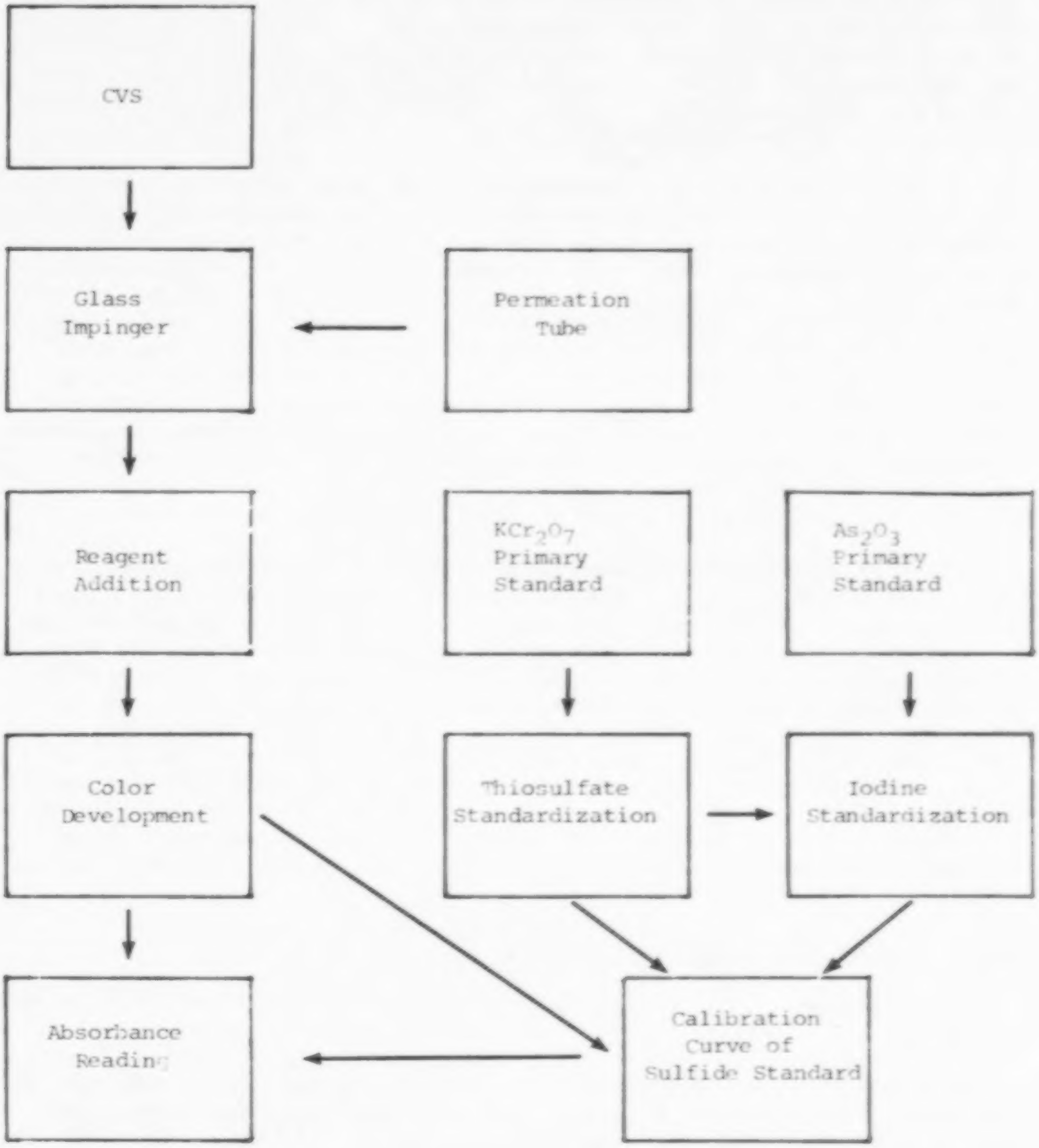

CVS
Glass Impinger
Permeation Tube
Reagent Addition
KCr_2O_7 Primary Standard
As_2O_3 Primary Standard
Color Development
Thiosulfate Standardization
Iodine Standardization
Absorbance Reading
Calibration Curve of Sulfide Standard

Figure 4. Hydrogen sulfide analysis flow schematic.

only once for the concentrated solution.

The dilute iodine solution (~0.01 N) prepared by diluting the concentrated iodine solution, is standarized against the previously standarized thiosulfate solution. To a beaker containing 25 mℓ of the dilute iodine solution, 10 mℓ of concentrated hydrochloric acid is added and the resulting solution is immediately titrated with the standarized thiosulfate solution. Just before the endpoint, starch is added to serve as an indicator. The dilute iodine solution should be standarized daily.

A Beer's Law curve is determined by adding 0.1, 0.25, 0.5, 1.0, 2.0, 3.0, and 5.0 mℓ of the sulfide standard solution to seven separate 100 mℓ volumetric flasks with each containing 10 mℓ of the absorbing reagent. A blank of the absorbing reagent is also prepared. A 10 mℓ portion of the amine solution is carefully poured down the side of each flask taking care not to introduce air bubbles. Then, 2 mℓ of the ferric ion solution are added and gently swirled. The contents are then diluted to 100 mℓ with vacuum boiled, deionized water and placed in the dark to develop for 30 minutes. This procedure should be repeated for the remaining flasks and the blank. The absorbance is read at 667 mm in a spectrophotometer against the reagent blank. The concentration of the samples are used to determine a best fit plot of the Beer's Law curve. In the higher concentration ranges, the curve is nonlinear and does not necessarily follow Beer's Law.

Another more efficient means of generating a Beer's Law curve requires the use of permeation tubes as a calibration standard. The calibration curve is generated by passing a diluent gas (preferably nitrogen) over the permeation tube and through a set of two impingers containing the buffered zinc acetate absorbing reagent. The length of time sampled is proportional to the concentration in the set of impingers. Not only is this a quick and efficient means of calibration, but it also takes into account the collection efficiency of the sampling technique. The samples are developed by the technique described above. The absorbance is read at 667 nm and this absorbance is used to determine the calibration curve. This best fit plot of the Beer's Law curve is used to determine the concentration of the samples. A quick and easy method of providing a daily calibration for the instrument can be obtained with this method.

Sample Acquisition and Color Development

To two clean glass impingers, 10 mℓ of acetate buffer and 40 mℓ of vacuum boiled, deionized water are added. These impingers are connected in series in the sampling system. During each test cycle, a portion of the diluted exhaust is bubbled through the absorbing reagent at a flow rate of 4.0 ℓ/min. Upon completion of each driving cycle, the impingers are replaced with fresh ones. To each of the collected samples, 10 mℓ of the amine solution is added through the top of the impinger and gently swirled. Then 6 mℓ (2 mℓ for samples from gasoline powered vehicles is sufficient) of the ferric ion solution is added in the same manner and mixed for 30 seconds. The solution is quantitatively transfered from the impingers to a 100 mℓ volumetric flask and diluted to 100 mℓ with vacuum boiled, deionized water.

The color development is complete in 30 minutes. The proceduer is repeated with the remaining samples. After 30 minutes, the absorbance is measured on a spectrophotometer at 667 nm against a reagent blank and the concentration determined from the calibration curve. The one and four cm curvettes are shown in Figure 5 and the spectrophotometer is shown in Figure 6.

This procedure is well documented and commonly used for the analysis of hydrogen sulfide. With a 4 cm cell, the minimum detectable quantity is on the order of 0.01 ppm. Extensive wet chemistry is involved to establish the calibration curve but the sample analysis time is minimal after color development.

CALCULATIONS

This procedure has been selected and developed to determine the quantity of hydrogen sulfide in dilute exhaust. A Hewlett-Packard 67 program was developed to reduce the time required for manual calculations. The derivation of the equations are given below and a copy of the steps in the program are shown in Figure 7.

Derivation of Equation

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F and pressure, 29.92"Hg, by use of the equacion

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92"Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92"Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

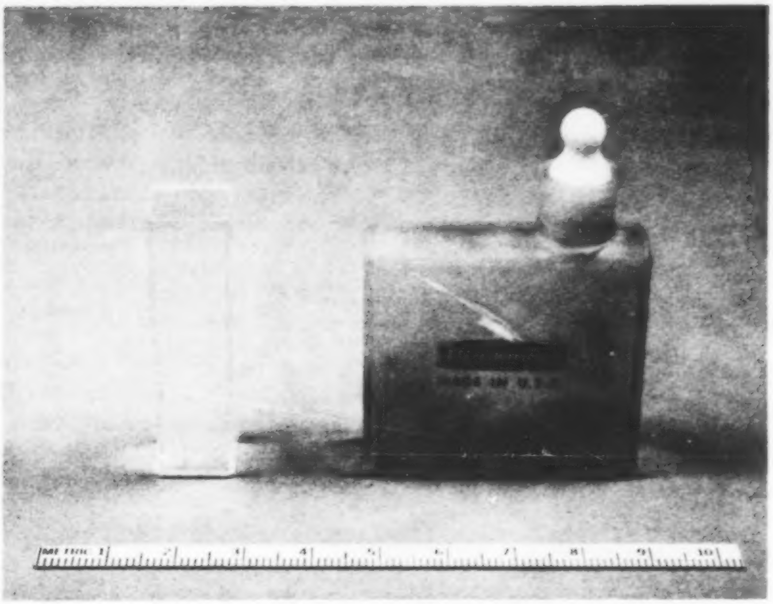
Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{"Hg}}$$

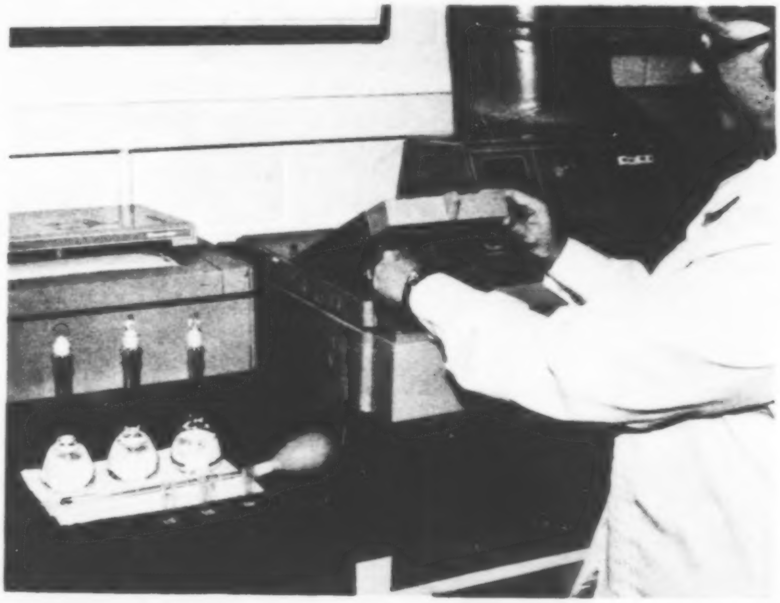
The next step converts the volume from cubic feet to cubic meters by use of the conversion factor; 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr}(m^3) = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)



One and four cm pathlength curvettes



Reading the absorbance

Figure 5. The analysis of hydrogen sulfide in exhaust.

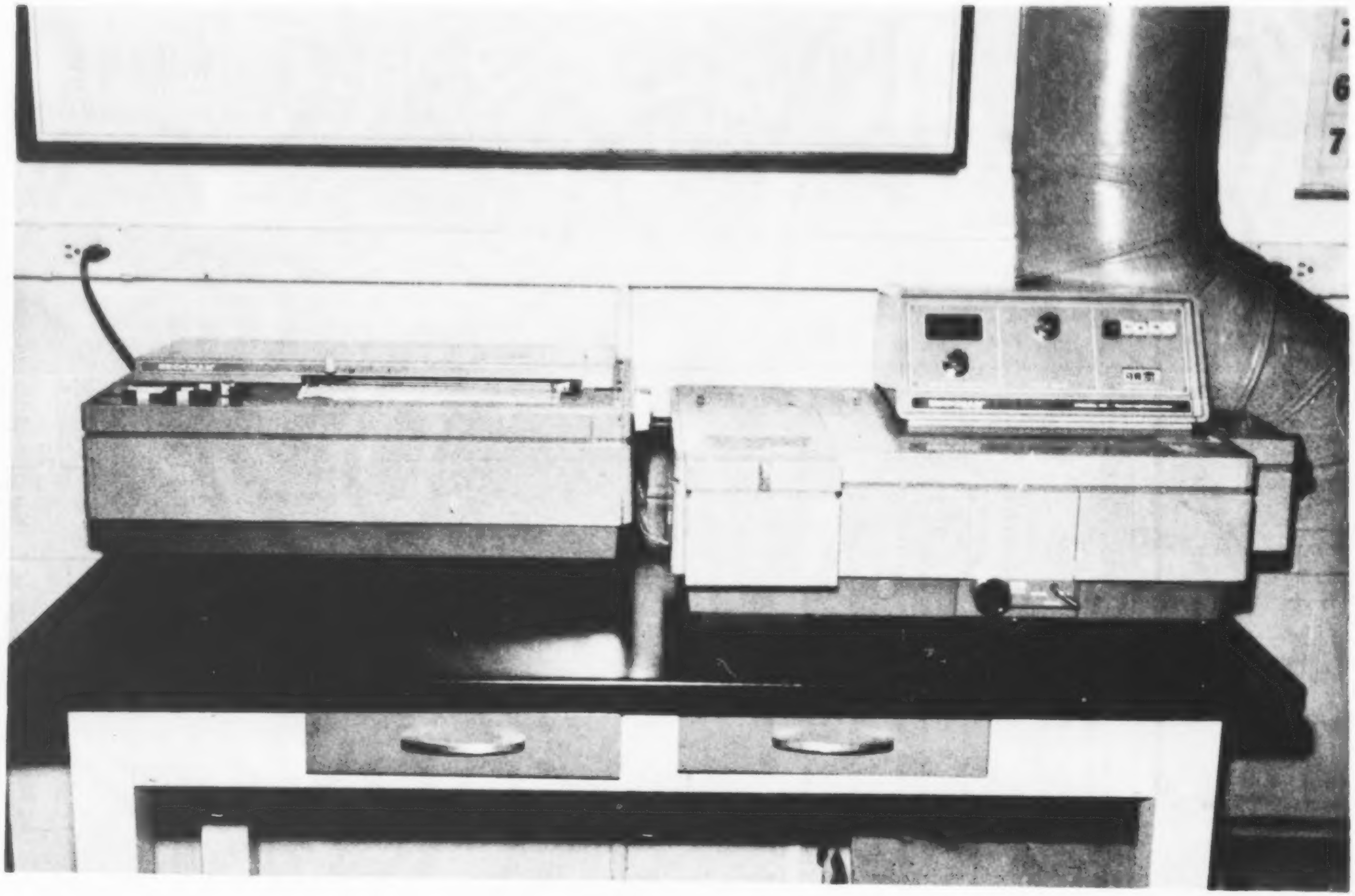
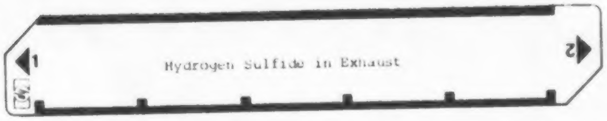


Figure 6. Beckman Model 25 spectrophotometer.

User Instructions



STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; Switch to Run				
0_2	Feed Card in from right to left side 1				
0_3	Set decimal place		g	Sci	
1	Input Sample Volume	ft^3	A		
2	Input Barometric Pressure	"Hg	R/S		
3	Input Sample Temperature	°F	R/S		
4	Input Total Volume of Solution	ml	R/S		
5	Input Sample Concentration Bubbler #1	$\mu gS^{2-}/ml$	R/S		
6	Output Sample Concentration Bubbler #1	$\mu gS^{2-}/ml$			$\mu gH_2S/m^3$
7	Input Sample Concentration Bubbler #2		R/S		
8	Output Sample Concentration Bubbler #2		R/S		$\mu gH_2S/m^3$
9	Output Total Sample Concentration Bubbler #1 + #2		R/S		$\mu gH_2S/m^3$
10	Output Sample Concentration		h	RTN	ppm

Figure 7. HP-67 User instructions

STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	In Sample Vol, ft^3
	2	02	
	÷	81	
	R/S	84	In Barometric, "Hg
	X	71	
	STO 1	33 01	
	R/S	84	In Sample Temp, °F
	4	04	
	6	06	
010	0	00	
	+	61	
	RCL 1	34 01	
	÷	81	
	R/S	84	In Total Vol of Sol mℓ
	X	71	
	STO 2	33 02	
	RCL 2	34 02	
	R/S	84	In Sample Conc, Bubbler #1, $\mu gS^{2-}/m\ell$
	X	71	
020	1	01	
	.	83	
	0	00	
	6	06	
	3	03	
	X	71	
	STO 3	33 03	Out Sample Conc, Bubbler #1, $\mu gH_2S/m^3$
	R/S	84	
	RCL 2	34 02	In Sample Conc, Bubbler #2, $\mu gS^{2-}/m\ell$
	X	71	
030	1	01	
	.	83	
	0	00	
	6	06	
	3	03	
	X	71	Out Sample Conc, Bubbler #2, $\mu gH_2S/m^3$
	R/S	84	
	RCL 3	34 03	
	+	61	
	R/S	84	Out Total Conc, $\mu gH_2S/m^3$
040	1	01	
	4	04	
	3	03	
	4	04	
	÷	81	
	R/S	84	Output ppm H_2S
	h RTN	35 22	
050			

STEP	KEY ENTRY	KEY CODE	COMMENTS
060			
070			
080			
090			
100			
110			

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A	B	C	D	E	I

Figure 7 (Cont'd). HP-67 program form

The concentration of sulfide ion in $\mu gS^{2-}/m\ell$ is obtained from the Beer's Law Plot of the absorbance. The concentration of hydrogen sulfide in $\mu gH_2S/m\ell$ is obtained by multiplying the concentration in $\mu gS^{2-}/m\ell$ by the ratio of the formula weight of hydrogen sulfide to the formula weight of sulfide ion.

$$\begin{aligned}\mu gH_2S/m\ell &= \mu gS^{2-}/m\ell \times \frac{\text{formula weight } H_2S(\mu g/\mu \text{ mole})}{\text{formula weight } S^{2-}(\mu g/\mu \text{ mole})}\\ &= \mu gS^{2-}/m\ell \times \frac{34.080\ \mu g\ H_2S/\mu \text{ mole}}{32.064\ \mu gS^{2-}/\mu \text{ mole}}\\ &= \mu gS^{2-}/m\ell \times 1.063\ \frac{\mu g\ H_2S}{\mu g\ S^{2-}}\end{aligned}$$

To obtain the total amount in µg of hydrogen sulfide, the concentration in $\mu gH_2S/m\ell$ is multiplied by the total volume of solution (TVS). This is the volume to which the absorbing solution, amine solution, and ferric ion solution have been diluted with deionized water. In this case the volume is 100 mℓ.

$$\begin{aligned}\mu gH_2S &= \mu gH_2S/m\ell \times TVS\\ &= \mu gH_2S/m\ell \times 100\ m\ell\\ &= \mu gS^{2-}/m\ell \times 1.063\ \frac{\mu gH_2S}{\mu gS^{2-}} \times 100\ m\ell\end{aligned}$$

(Equation 2)

To obtain $\mu gH_2S/m^3$, Equation 2 is divided by Equation 1 to give:

$$\mu gH_2S/m^3 = \frac{\mu gS^{2-} \times 1.063\ \frac{\mu gH_2S}{\mu gS^{2-}} \times 100\ m\ell \times T_{exp} \times 29.92''Hg \times 35.31\ ft^3/m^3}{P_{exp}\ (''Hg) \times V_{exp}\ (ft^3) \times 528^\circ}$$

(Equation 3)

To find the concentration of hydrogen sulfide in ppm, the density of hydrogen sulfide at 68° and 29.92"Hg is needed. The fifth edition of the Matheson Gas Data Book lists the density of hydrogen sulfide at 0°C and 1 atmosphere at 1.5392 g/ℓ. If the volume of 1ℓ of gas is corrected for temperature,

$$V = 1\ell \times \frac{528^\circ R}{(32^\circ F + 460} = 1.073\ \ell$$

it can be divided into the weight of the gas to give the density at 68°F

$$\frac{1.5392\ g}{1.073\ \ell} = 1.434\ g/\ell = 1434\ \mu g/m\ell$$

To obtain the concentration of hydrogen sulfide in ppm, the concentration in $\mu g/m^3$ is divided by the density in $\mu g/m\ell$

$$\text{ppm} = \mu g\ H_2S/m^3 \div \mu g/m\ell = \frac{m\ell}{m^3}$$

(Equation 4)

At this point, the concentration can be expressed in $\mu gH_2S/m^3$ (Equation 3) and ppm (Equation 4) at 68°F and 29.92"Hg from the raw data.

Sample Calculations

Assume that a set of six samples was taken from dilute exhaust during several different driving cycles. The volume of dilute exhaust sampled during the first test was 3.185 ft^3 at a barometric pressure of 29.41"Hg and a temperature of 77°F. The analysis was conducted and Bubbler #1 was found to contain 9.2 $\mu gS^{2-}/m\ell$ while Bubbler #2 contained 0.8 $\mu gS^{2-}/m\ell$

For Bubbler #1

$$\mu gH_2S/m^3 = \frac{\mu gS^{2-}/m\ell \times 1.063\ \frac{\mu gH_2S}{\mu gS^{2-}} \times 100\ m\ell \times T_{exp} \times 29.92''Hg \times 35.31\ ft^3/m^3}{P_{exp}\ (''Hg) \times V_{exp}\ (ft^3) \times 528°R}$$

$$= \frac{9.2\ \mu gS^{2-}/m\ell \times 1.063\ \mu gH_2S/\mu gS^{2-}}{29.41''\ Hg \times 3.185\ ft^3}$$

$$\times \frac{100\ m\ell \times (460 + 77°F) \times 29.92''Hg \times 35.31\ ft^3/m^3}{528°R}$$

$$= 11218\ \mu g/m^3$$

The concentration for Bubbler #2 is calculated in the same manner using the appropriate concentration in $\mu gS^{2-}/m\ell$

For Bubbler #2

$$\mu gH_2S/m^3 = \frac{0.8\ \mu gS^{2-}/m\ell \times 1.063\ \mu gH_2S/\mu gS^{2-}}{29.41''\ Hg \times 3.185\ ft^3}$$

$$\times \frac{100\ m\ell \times (460 + 77°F) \times 29.92''Hg \times 35.31\ ft^3/m^3}{528°R}$$

$$= 975\ \mu g/m^3$$

$$\text{Total}\ \mu g\ H_2S/m^3 = \text{Conc (Bubbler \#1)} + \text{Conc (Bubbler \#2)}$$

$$= 11218 + 975$$

$$= 12193\ \mu g/m^3$$

$$\text{ppm } H_2S = \mu g H_2S/m^3 \div \text{density } \mu g/m\ell$$

$$= 12193 \ \mu g H_2S/m^3 \div 1434 \ \mu g/m^3$$

$$= 8.50 \text{ ppm}$$

The values for the six sets of sample data are given in Figure 8 along with the data sheet. The calculations were carried out manually and with the HP-67 program. The program will be used to calculate both $\mu g H_2S/m^3$ and ppm H_2S and to insure rapid data turnaround. The values used in these calculations were picked at random and may not represent the expected values in exhaust.

LIST OF EQUIPMENT

The equipment required in this analysis is divided into two basic categories. The first category involves the sample acquisition using the glass impingers. The second category contains equipment related to the analysis of the sample once it has been obtained. The individual items in each category are listed below:

Sample Acquisition

1. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/min.
2. Glass impingers, Ace Glass Products, Catalog No. 7530-11, 29/42 bottler joints, 18/7 arm joints.
3. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range.
4. Regulating valve, Nupro 4MG, stainless steel.
5. Dry gas meter, American Singer Corporation, Type Al-120, 60 CFH capacity.
6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 3/16" ID.
7. Teflon solenoid valve, The Fluorocarbon Company, Model DV2-144NCA1.
8. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.
9. Drying tube, Analabs, Inc., Catalog No. HGC-146, 6" long, 1/4" brass fittings.
10. Digital readout for dry gas meter.
11. Miscellaneous electrical switches, lights, wriings, etc.

SWRI PROJECT NO. 11-1234 TEST NO. 001 TEST DATE: 11-10-79 VEHICLE: Practice

FUEL: EM-237 CVS NO. 3 TUNNEL SIZE: 18" DRIVER: D.A.T. MILES: 1000

SAMPLE COLLECTION BY: G.O. CHEMICAL ANALYSIS BY: W.M.S. CALCULATIONS BY: L.R.S.

GENERAL COMMENTS:

Test No.	1	2	3	4	5	6
Driving Cycle	Cold FTP	Hot FTP	SET-7	HFET	NYCC	Background
Volume, Ft^3	3.185	3.486	3.508	1.926	1.525	15.826
B.P., "Hg	29.41	28.66	29.33	29.40	29.10	29.04
Temp. °F	77	75	80	85	90	77
Total Vol. of Solution, mℓ	100	100	100	100	100	100
Sample Conc-Bub.#1, $\mu g S^{2-}/m\ell$	9.2	7.3	10.4	3.1	1.0	0.5
Sample Conc-Bub.#1, $\mu g H_2S/m^3$	11200	8310	11600	6340	2630	124
Sample Conc-Bub.#2, $\mu g S^{2-}/m\ell$	0.8	0.2	1.1	0.3	0.1	0.1
Sample Conc-Bub.#3, $\mu g H_2S/m^3$	975	228	1230	614	263	24.8
Total Sample Conc, $\mu g H_2S/m^3$	12200	8540	12800	6960	2900	149
Total Conc. ppm H_2S	8.50	5.95	8.95	4.85	2.02	0.10

Figure 8. Raw data sheet for hydrogen sulfide analysis.

12. Six-channel digital thermometer, Analog Devices, Model 2036/J/1.

13. Iron/Constantan Type J, Thermo Sensors Corporation, single thermocouple, 1/4" OD stainless steel metal sheath.

14. Modified 25 mm A-H Microanalysis filter holder, Millipore, Catalog #XX50 020 00.

15. Fluoropore 25 mm filters, Millipore, Catalog #FHLP 025 00, 0.5 micron pore size.

16. Flexible heavy insulation heating tape, Briskeat®, width 1/2 inch, length 48 inches.

17. Temperature Controller, Athena, 100-600 °F

18. Heated TFE Teflon hose, Technical Heaters, Inc., 5' x 1/4", temperature limit 400°F.

Sample Preparation

1. Pipet-aid, Order No. JX-7290.
2. Class A, 10 mℓ volumetric pipets.
3. Class A, 15 mℓ volumetric pipets.
4. Class A, 20 mℓ volumetric pipets.
5. Class A, 25 mℓ volumetric pipets.
6. Class A, 100 mℓ volumetric flask.
7. Class A, 500 mℓ volumetric flask.
8. Class A, 1000 mℓ volumetric flask.
9. Class A, 25 mℓ burets with Teflon Stopcock.
10. Class A, 100 mℓ graduated cylinder.
11. Micro burets, 5 mℓ Teflon stopcock.
12. Erlenmeyer flask, 250 mℓ.
13. Erlenmeyer flask, 500 mℓ.
14. Dropping bottle, 60 mℓ ground glass pipet and rubber bulb.
15. Beaker, 100 mℓ.

16. Repipet dispenser, 2 mℓ.

17. Repipet dispenser, 10 mℓ.

18. Centrifuge tube, 15 mℓ.

19. Watch glass.

Instrumental Analysis

1. Beckman Model 25 spectrophotometer with recorder.

2. One cm pathlength disposable curvettes, CI regular.

3. Beckman UV silica cell, 40mm pathlength, No. 580016.

LIST OF REAGENTS

This procedure requires the sample collection in glass impingers with a buffered zinc acetate absorbing solution (0.25 M zinc acetate and 0.10 M sodium acetate). An amine reagent (0.005 M, N,N dimethyl-para-phenylene diamine sulfate and 3.50 M sulfuric acid) and a ferric ion solution (0.25 M ferric ammonium sulfate and 0.5 M sulfuric acid) are mixed with the absorbing solution. Sodium sulfide is used as the standard. An iodometric titration is used to standarize the sodium sulfide. All of the reagents used in preparing these solutions are listed below along with the manufacturer and the quality.

1. Zinc acetate, dihydrate formula weight = 219.49; chemical formula = $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, crystal, "Baker Analyzed" reagent.

2. Sodium acetate, anhydrous formula weight = 82.03; chemical formula= $NaC_2H_3O_2$, analytical reagent grade, powder, Mallinckrodt Code 7372.

3. N,N dimethyl-para-phenylene diamine sulfate, formula weight = 370.47; chemical formula = $(NH_2C_6H_4N(CH_3)_2)_2 \cdot H_2SO_4)$, 98 percent minimum by titration and spectro analysis, Eastman Code 1333.

4. Sulfuric acid, formula weight = 98.08; chemical formula = H_2SO_4, ACS analytical reagent grade, Mallinckrodt Code 2876.

5. Ferric ammonium sulfate, formula weight = 482.19; chemical formula= $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$, ACS analytical reagent grade, crystals, Mallinckrodt Code 5064.

6. Sodium sulfide, formula weight = 240.18; chemical formula = $Na_2S \cdot 9H_2O$, ACS analytical reagent grade, crystals, Mallinckrodt Code 8044.

7. Iodine, formula weight = 253.81; chemical formula = I_2, ACS analytical reagent grade, resublimed, Mallinckrodt Code 1008.

8. Hydrochloric acid, formula weight = 36.46; Chemical formula = HCl, ACS reagent, assay 36.5-38.0 percent HCl, Eastman Code 13061.

9. Sodium thiosulfate, formula weight = 248.18; chemical formula = $Na_2S_2O_3 \cdot 5H_2O$, ACS analytical reagent grade, crystals, Mallinckrodt Code 8100.

10. Starch soluble; chemical formula = $(C_6H_{10}O_5)n$, certified ACS, powder, Fisher Code S-516.

11. Arsenic trioxide primary standard, formula weight = 197.82; chemical formula = As_2O_3, powder, ACS analytical reagent, Mallinckrodt Code 3668.

12. Potassium iodine, formula weight = 166.01; chemical formula = KI, compacted crystal, "Baker Analyzed" reagent.

13. Sodium hydroxide pellets, formula wieght = 40.00; chemical formula= NaOH, caustic soda, ACS analytical reagent grade, Mallinckrodt Code 7708.

14. Sodium bicarbonate, formula weight = 84.01; chemical formula = $NaHCO_3$, powder, ACS analytical reagent grade, Mallinckrodt Code 7412.

15. Sodium carbonate anahydrous powder, formula weight = 105.99; chemical formula = Na_2CO_3, ACS analytical reagent grade, Mallinckrodt Code 7521.

16. Potassium dichromate, crystal, primary standard, formula weight = 294.22; chemical formula = $K_2Cr_2O_7$, "Baker Analyzed" reagent.

17. Litmus test paper, blue, reagent ACS, Fisher Code 14-875.

18. Glycerol, formula weight = 92.10; chemical formula = $HOCH_2CH(OH)CH_2OH$, ACS analytical reagent, Mallinckrodt Code 5092.

PREPARATION OF REAGENTS

The various reagents needed for the analysis of hydrogen sulfide can be divided into two separate categories. The first category includes the reagents for sample acquisition and color development. The other category encompasses the standard solutions and solutions used for standardization. The chemicals used to make these solutions are ACS analytical reagent grade with the exception of potassium dichromate and arsenic trioxide which are a primary reagent grade.

Sample Acquisition and Color Development

Absorbing Reagent - The absorbing reagent is prepared by dissolving 54.9 g (0.25 mole) of zinc acetate, 8.2 g (0.10 mole) of sodium acetate, and 40 mℓ (0.56 mole) gylcerol, in vacuum boiled, deionized water and diluting to 1 liter. A 2 mℓ portion of 0.05 M sodium sulfide solution is added dropwise to the diluted solution with vigorous shaking. This removes traces of heavy metals by precipating them as their insoluble sulfides. This solution is then set aside overnight. The resulting solution is filtered through a fine textured paper with the first 50 mℓ portion being discarded. This solution is stable for at least one (1) week. A gradually developing cloudiness is of no consequence.

Amine Solution - A 0.005 M solution is prepared by dissolving 0.93 g of N,N dimethyl-para-phenylene diamine sulfate in 75 mℓ of deionized water. Then, 197 mℓ of concentrated sulfuric acid is slowly added and the mixture is allowed to cool. The resulting solution is diluted to 1 liter with deionized water. This solution is stable for about six (6) months.

Ferric Ion Solution - The ferric ion solution is prepared by dissolving 120.6 g (0.25 mole) of ferric ammonium sulfate in 750 mℓ of deionized water. A 27 mℓ portion of concentrated sulfuric acid is added and the solution is allowed to cool before diluting to 1 liter with deionized water. The solution is stable for one (1) month.

Standards and Standarization Solutions

Sulfide Standard Solution - Approximately 8 g (0.03 mole) of sodium sulfide is rinsed with vacuum boiled, deionized water to remove traces of sulfide from the surface of the crystals. The crystals are then dissolved in vacuum boiled, deionized water and diluted to 1 liter to give a concentrated solution. A more dilute solution of sulfide ion is prepared by diluting 10 mℓ of the concentrated solution to 1 liter with vacuum boiled, deionized water. This solution is standardized by iodometric titration. The approximate concentration is 10 ppm sulfide ion by weight. This solution should be prepared immediately before use.

Thiosulfate Standard Solution - Approximately 2.5 g (0.01 mole) of sodium thiosulfate is dissolved in 500 mℓ of freshly vacuum boiled, deionized water in a 1 liter volumetric flask. A 0.1 g (0.001 mole) portion of sodium carbonate is added and the solution is stirred until dissolved. The solution is then diluted to 1 liter and stored in the dark. Addition of a small amount of sodium carbonate pervents the formation of hydrogen sulfite ion from thiosulfate ion in the presence of acid. The addition of such substances as chloroform, sodium benzoate, or mercury (II) iodine inhibits the growth of bacteria. This solution is stable for several weeks but should be discarded if it becomes turbid. It is standarized with a potassium dichromate primary standard.

Starch Indicator - The indicator is prepared by making a paste of 0.5 g of soluble starch in 2 or 3 mℓ of boiling water. The resulting slurry is slowly poured into 50 mℓ of boiling deionized water and heated until clear (about 2-3 minuted). The solution is then cooled and centrifuged for several minutes. The supernatant liquid is decanted into a clean, 60 mℓ reagent bottle equipped with a pipet. This aqueous starch solution will decompose due to bacterial action in several days. This can be prevented by storing the indicator under sterile conditions, the addition of mercury (II) iodide to inhibit the bacterial action, or by preparing fresh daily.

Iodine Solution - About 25 g (0.15 mole) of potassium iodide is dissolved in 10 mℓ of deionized water. Then, 12.7 g (0.05 mole) of iodine crystals are added and dissolved with occasional stirring. The solution is filtered and diluted to 1 liter with deionized water. The resulting solution is approximately 0.1 N and is used to prepare the 0.01 N solution. The 0.1 N solution is standarized against arsenic trioxide. The dilute iodine solution is prepared by diluting 10 mℓ of the 0.1 N solution to 100 mℓ with deionized water. This solution is standarized with a previously standarized thiosulfate solution. The dilute iodine solution is prepared and standarized daily because of the volatility of iodine and oxidation by dissolved oxygen.

REFERENCES

Stecher, P.G., (Ed.), The Merck Index, An Encyclopedia of Chemicals and Drugs, 8th Edition, Merck and Co., Inc. Rahway, N.Y., 1968, pg. 545.

Braker, W. and Mossman, A.L., Matheson Gas Data Book, 5th Edition, East Rutherford, N.J., 1971, pg. 319.

Bethea, R.M., J. Air Poll. Cont. Assoc., Vol. 23, pg. 710, 1973.

Bamesberger, W.L. and Adams, D.F., Tappi, Vol. 52, pg. 1302, 1969.

Falgout, D.A. and Harding, C.I., J. Air Poll. Cont. Assoc., Vol. 18, pg. 15, 1968.

Biles, B., Brown, C., Nash, T., J. Phys, E.: Scientific Instruments, Vol. 7, pg. 309, 1974.

Wellinger, R. and Fiever, P.M., Am. Ind. Hyg. Assoc. J., Vol. 35, pg. 730, 1974.

Natusch, D.F.S., Sewell, J.R., and Tanner, R.L., Anal. Chem., Vol. 46, pg. 410, 1974.

"Trace Sulfue in Hydrocarbons by the Raney Nickel Method," Analytical Method Information, Analytical and Informational Division, Exxon Research and Engineering Co., September 1975.

Pierce, R.W., ISA Tran., Vol. 13, pg. 291, 1974.

Axelrod, H.D., Cary, J.H., Bonelli, J.E., and Lodge, J.P., Anal. Chem., Vol. 41, pg. 1959, 1969.

Natusch, D.F.S., Klonis, H.B., Axelrod, H.D., Teck, R.J., Lodge, Jr., J.P., Anal. Chem., Vol. 44, pg. 2067, 1972.

Bock, R. and Puff, H., Z. Anal. Chem., Vol. 240, pg. 381. 1968.

Nauman, R. and Weber, C., Z. Anal. Chem., Vol. 253, pg. 111, 1971.

Ehman, D.L., Analy. Chem., Vol. 48, pg. 918. 1976.

Hseu, T.M. and Rechnitz, G.A., Anal. Chem., Vol. 40, No. 7, pg. 1054.

Hseu, T.M. and Rechnitz, G.A., Anal.Chem., Vol. 40, No. 7, pg. 1054, 1968; see also correction: Ibid. Vol. 40, No. 11, pg. 1661, 1968.

Baumann, E.W., Anal. Chem., Vol. 46, No. 9, pg. 1345, 1974.

Blanchette, A.R., and Copper, A.D., Anal. Chem., Vol. 48, pg. 729, 1976.

"Analysis of H_2S and SO_2 in the ppb Range," Bulletin 722C, Supelco, Inc., Belefonte, Pa., 1975.

Setter, J.R., Sedlak, J.M., Blurton, K.F., J. Chromatog. Sci,, Vol. 15, pg. 125, 1977.

Greer, D.G. and Bydalek, T.J., Environ. Sci. Tech., Vol. 7, pg. 153, 1973.

Obermiller, E.L. and Charlier, G.O., Anal. Chem., Vol. 39, pg. 397, 1967.

Bethea, R.M. and Meador, M.C., J. Chromatog. Sci., Vol. 7, pg. 655, 1969.

Jones, C.N., Anal. Chem., Vol. 39, pg. 1858, 1967.

Wilhite, W.F. and Hollis, O.L., J. Gas Chromatog., Vol. 6, pg. 84, 1968.

Thornsberry Jr., W.L., Anal. Chem., Vol. 43, pg. 452, 1971.

Adams, D.F., Jensen, G.A., Steadman, J.P., Koppe, R.K., and Robertson, T.J., Anal. Chem., Vol. 38, pg. 1094, 1966.

Martin, R.L. and Grant, J.A., Anal. Chem., Vol. 37, pg. 644, 1965.

Adams, D.F., Bamesberger, W.L., and Robertson, T.J., J. Air Poll. Cont. Assoc., Vol. 18, pg. 145, 1968.

Levaggi, D.A., Siu, W., and Fedlstein, M., Advances in Automated Analysis, Vol. 8, pg. 65, 1972.

"Hydrogen Sulfide in Air Analytical Method," H.L.S., Vol. 12, pg. 362, 1975.

Bamesberger, W.L. and Adams, D.F., Environ. Sci. Tech., Vol. 3, pg. 258, 1969.

Gustafsson, L., Talanta, Vol. 4, pg. 227, 1960.

Moest, R.R., Anal. Chem., Vol. 47, pg, 1204, 1975.

Buck, M. and Gies, H., Staub, Vol. 26, pg. 1966.

Jacobs, M.B., Braverman, M.M., and Hochheiser, S., Anal. Chem., Vol. 29, pg. 1349, 1957.

Cave, G.C.B., Tappi, Vol. 46, pg. 1, 1963.

Budd, M.S. and Bewick, H.A., Anal. Chem., Vol. 24, pg. 1536, 1952.

Bostrom, C., Air and Water Poll. Int. J., Vol. 10, pg. 435, 1966.

Flamm, D.L. and James, R.E., Environ. Sci. Tech. pg. 159, 1975.

APPENDIX H

AMMONIA PROCEDURE

THE MEASUREMENT OF AMMONIA IN EXHAUST

The measurement of ammonia in dilute automotive exhaust is accomplished by bubbling dilute exhaust through glass impingers containing dilute sulfuric acid. Ammonia is complexed by the acid to form a stable sulfate salt which remains in solution. The exhaust sample is collected continuously during a test cycle. A sample from the impinger is analyzed for ammonia by the use of an Ion Chromatograph. The concentration of ammonia is calculated by comparison to a standard.

SAMPLING SYSTEM

Two glass impingers in series, each containing 25 mℓ of 0.01 N sulfuric acid, are used to collect exhaust samples for the analysis of ammonia. A flow schematic of the sample collection system is shown in Figure 1. The two impingers together trap approximately 99+ percent of the ammonia. The temperature of the impinger is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4 ℓ/minute by the sample pump. A dry gas meter is used to determine the total flow through the impingers during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allows continuous monitoring of the sample flow to insure proper flow rates during sampling. When sampling diesel fueled vehicles, a filter, located between the on-off solenoid valve and the dilution tunnel, is used to prevent diesel particulate from contaminating the sampling system. The line connecting the filter to the dilution tunnel and the line connecting the filter to the solenoid valve are heated to 175°F in order to prevent water from condensing in the sample lines. Several views of the sampling system are shown in Figure 2.

PROCEDURE

Ammonia in exhaust is collected in two impingers connected in series with each impinger containing 25 mℓ of 0.01 N H_2SO_4. These two impingers trap 99+ percent of the ammonia. After the acidification of ammonia which takes place at ice bath temperatures (0-5°C), the ammonia samples are poured into polypropylene bottles and stored. The samples are then ready for NH_4^+ analysis on the ion chromatograph (Figure 3). Approximately 2 mℓ of sample are used to purge a 0.1 mℓ sample loop, after which 0.1 mℓ of sample is injected into the eluent stream. Separation of ions occurs in the separator (analytical) column. The background conductance of the eluent (0.0075 N HNO_3) is neutralized in the suppressor solumn. The 9 x 250 glass cation suppressor column is packed with AG- X10, a strong base ion exchange resin in the hydroxide form. A patented resin containing a sulfonic acid cation exchanger is packed into

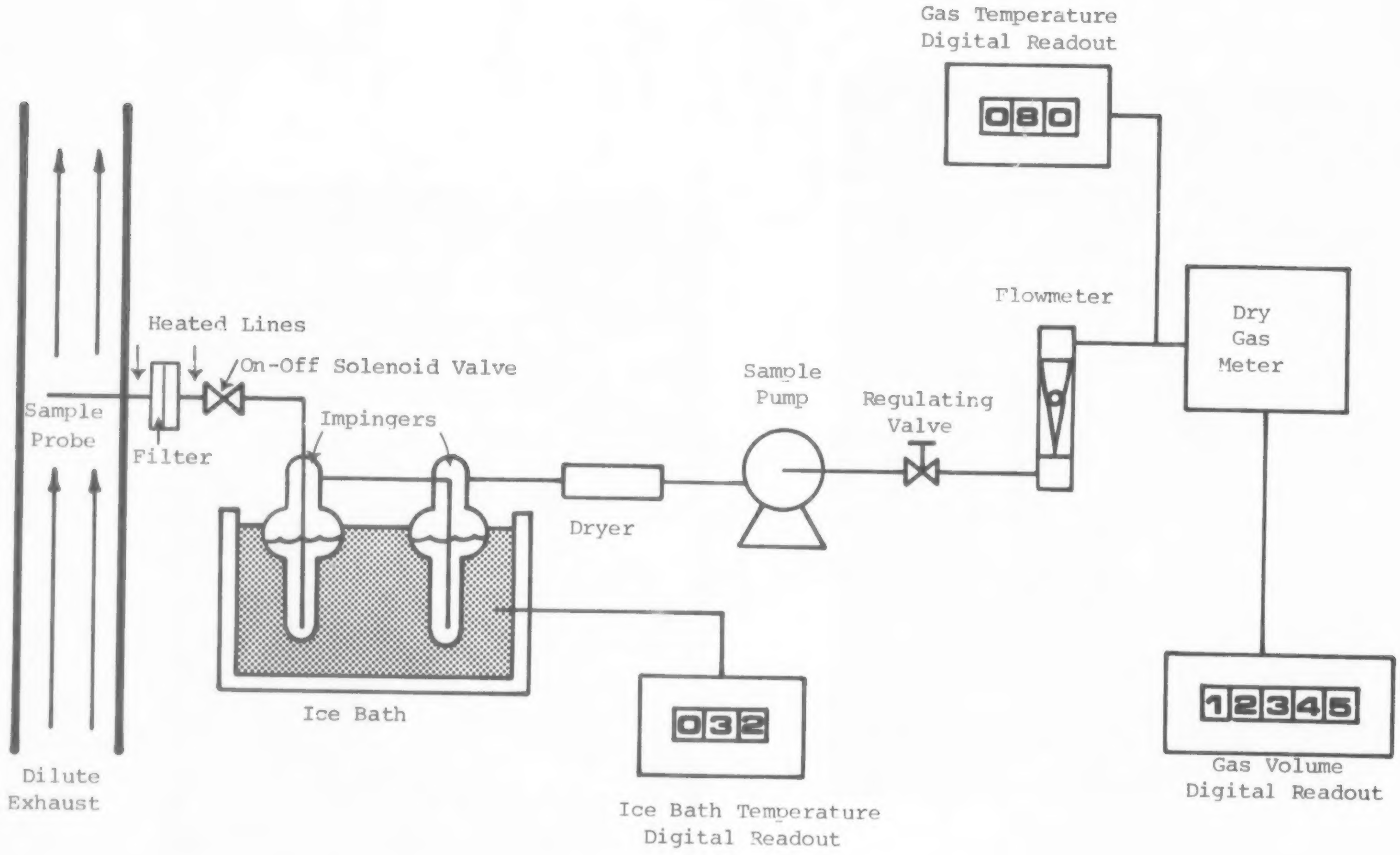
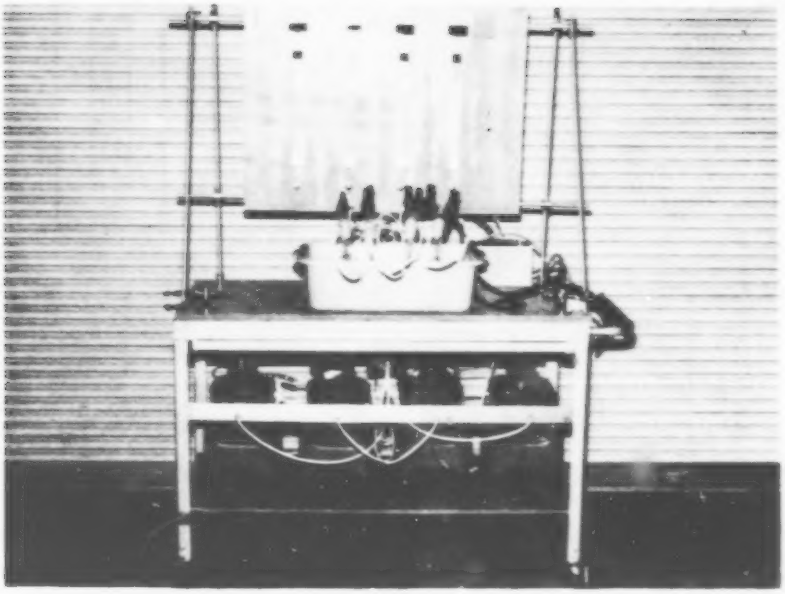
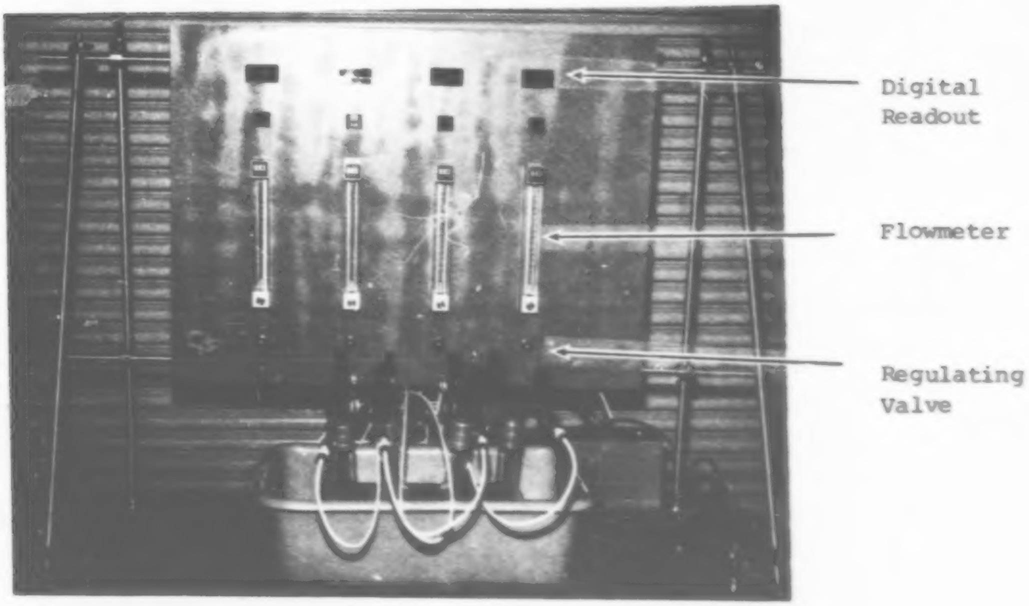

Gas Temperature
Digital Readout
080
Flowmeter
Dry
Gas
Meter
Heated Lines
On-Off Solenoid Valve
Sample
Pump
Regulating
Valve
Sample
Probe
Filter
Impingers
Dryer
Ice Bath
032
12345
Dilute
Exhaust
Ice Bath Temperature
Digital Readout
Gas Volume
Digital Readout

Figure 1. NH_3 sample collection flow schematic.

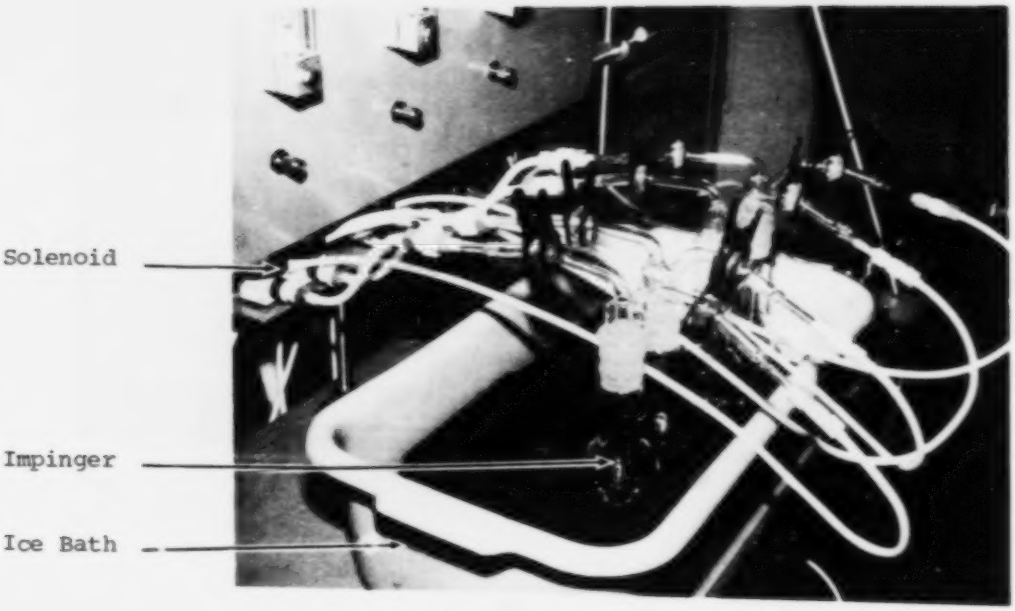


Front View

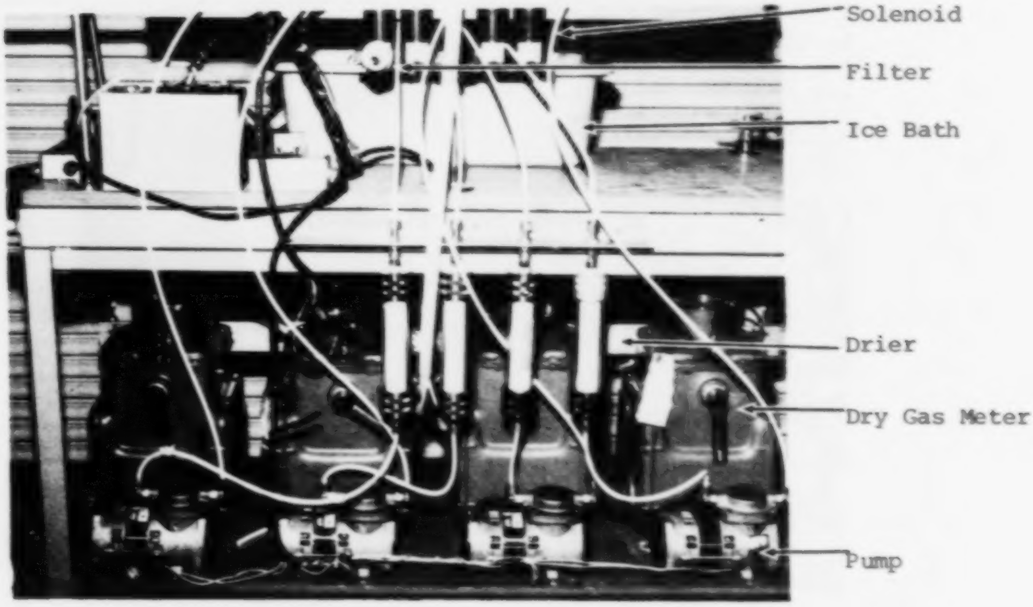

Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. Ammonia sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). Ammonia sampling system.

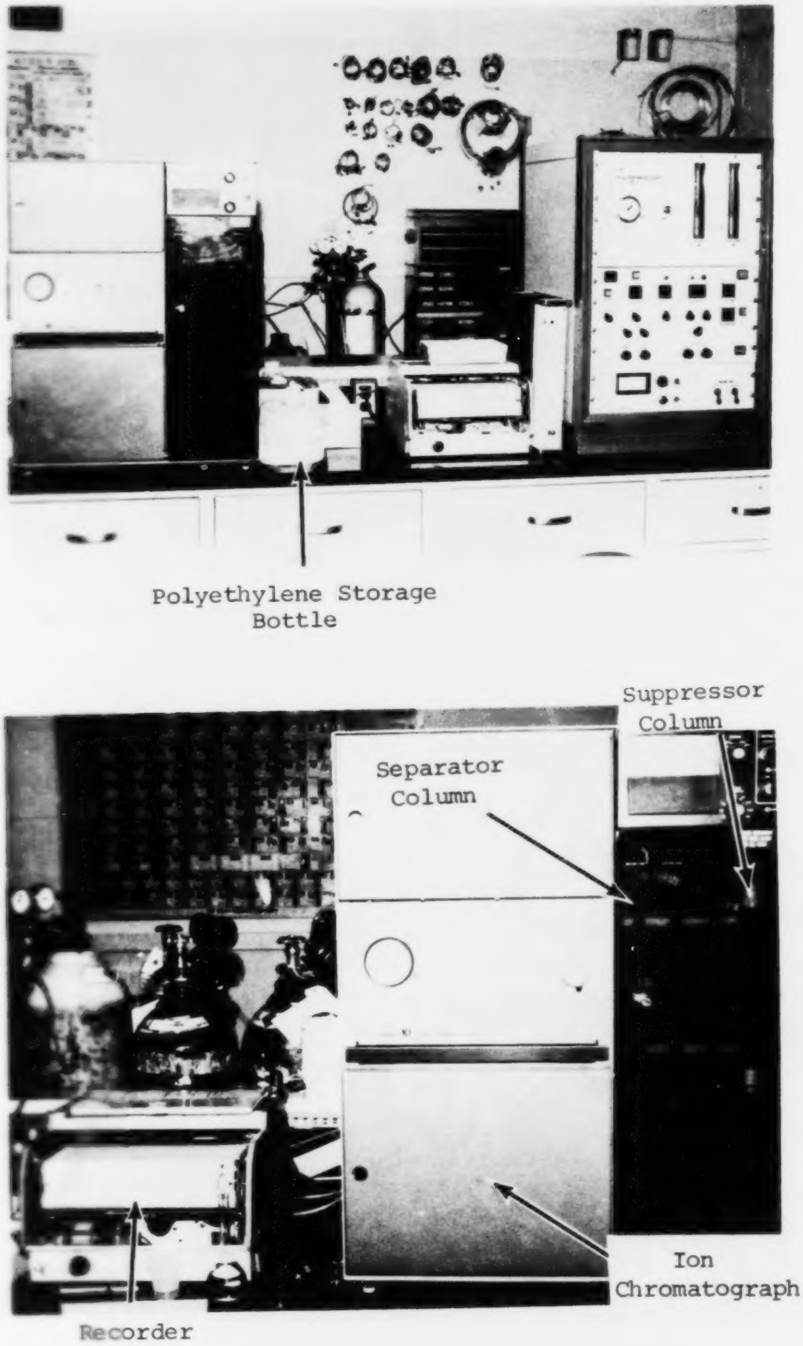

Polyethylene Storage Bottle
Suppressor Column
Separator Column
Ion Chromatograph
Recorder

Figure 3. NH_3 ion chromatograph.

the 6 x 250 mm glass separator column and the 3 x 150 mm precolumn. After the cations are separated in the analytical column they pass into the suppressor column in the dilute nitric acid eluent. The hydroxide form of the suppressor resin neutralizes the acid and then converts the cations to their hydroxides.

$$HNO_3 + \text{Resin} - OH \rightleftharpoons \text{Resin} - NO_3 + H_2O$$

$$\text{Cation}^+ + NO_3^- + \text{Resin} - OH \rightleftharpoons \text{Resin} - NO_3 + \text{Cation}^+ + OH^-$$

The conductivity cell produces a signal for the species of interest, NH_4OH, but doesn't "see" the neutralized eluent, deionized water. Conductance is interpreted as a recorder trace (chromatogram) or as peak area by the Hewlett-Packard 3354 computer system. Figure 4 depicts the analysis flow schematic of the entire ammonia procedure. Two chromatograms produced by the analysis of a sample and a standard are shown in Figures 5 and 6. After the 12-20 minute analysis the collection conditions and areas of sample and standard are used to compute NH_3 concentration from a Hewlett-Packard 67 program.

CALCULATIONS

The purpose of this procedure is to determine the concentration of ammonia in automotive exhaust. To do this, ammonia is converted to the protonated form, NH_4^+, which is measured on the ion chromatograph. The calculations involve correcting the measured concentration of NH_4^+ to NH_3 at a desired temperature and pressure. These calculations are carried out in a minimum amount of time by using a Hewlett-Packard 67 calculator program. A copy of the program is shown in Figure 7. Information from the data sheet (Figure 8) is entered into the calculator and the ammonia concentration in $\frac{\mu g\ NH_3}{m^3}$ and ppm NH_3 is computed. For illustration, two examples using information from the data sheet will be included at the end of this section.

The first step in the derivation of the equation for the calculation of ammonia concentration involves comparison of the sample to a standard of known concentration. A standard with peak size close to that of the sample is selected.

$$\frac{PA_{st}}{C_{st}} = \frac{PA_{sa}}{C_{sa}} \qquad C_{sa} = \frac{PA_{sa} \times C_{st}}{PA_{st}}$$

where PA_{st} = peak area of the standard

PA_{sa} = peak area of the sample

C_{st} = concentration of the standard $(\frac{\mu g\ NH_4^+}{m\ell})$

C_{sa} = concentration of the sample $(\frac{\mu g\ NH_4^+}{m\ell})$

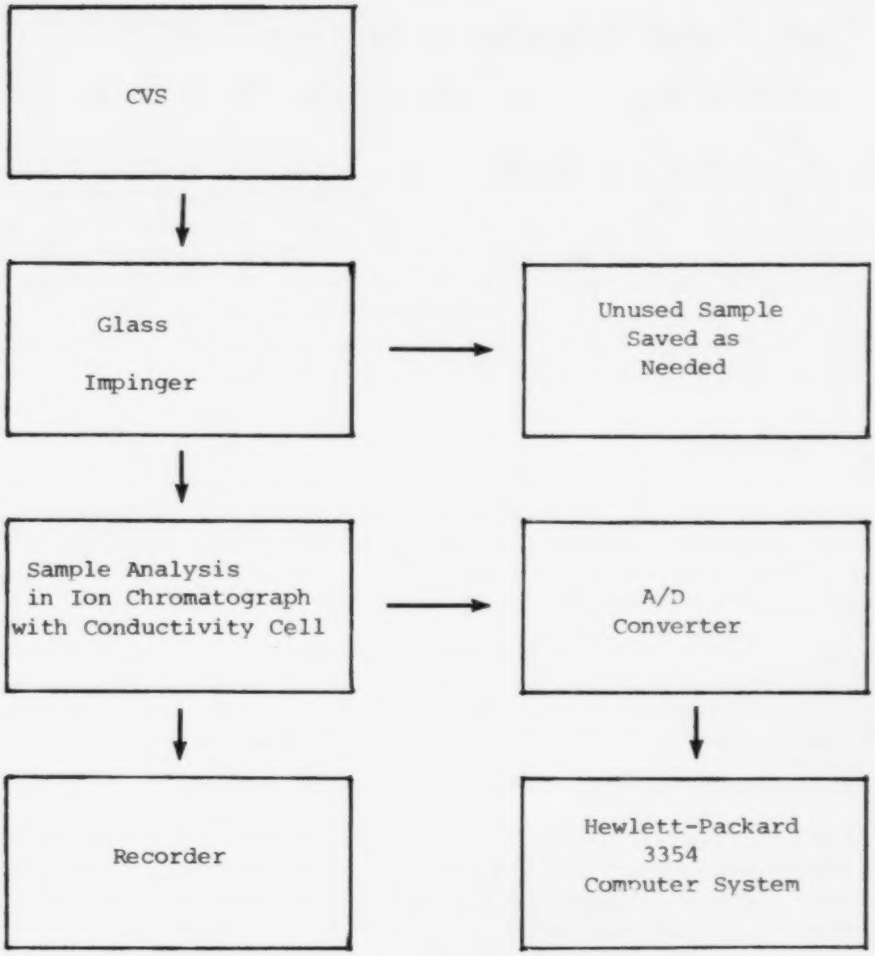
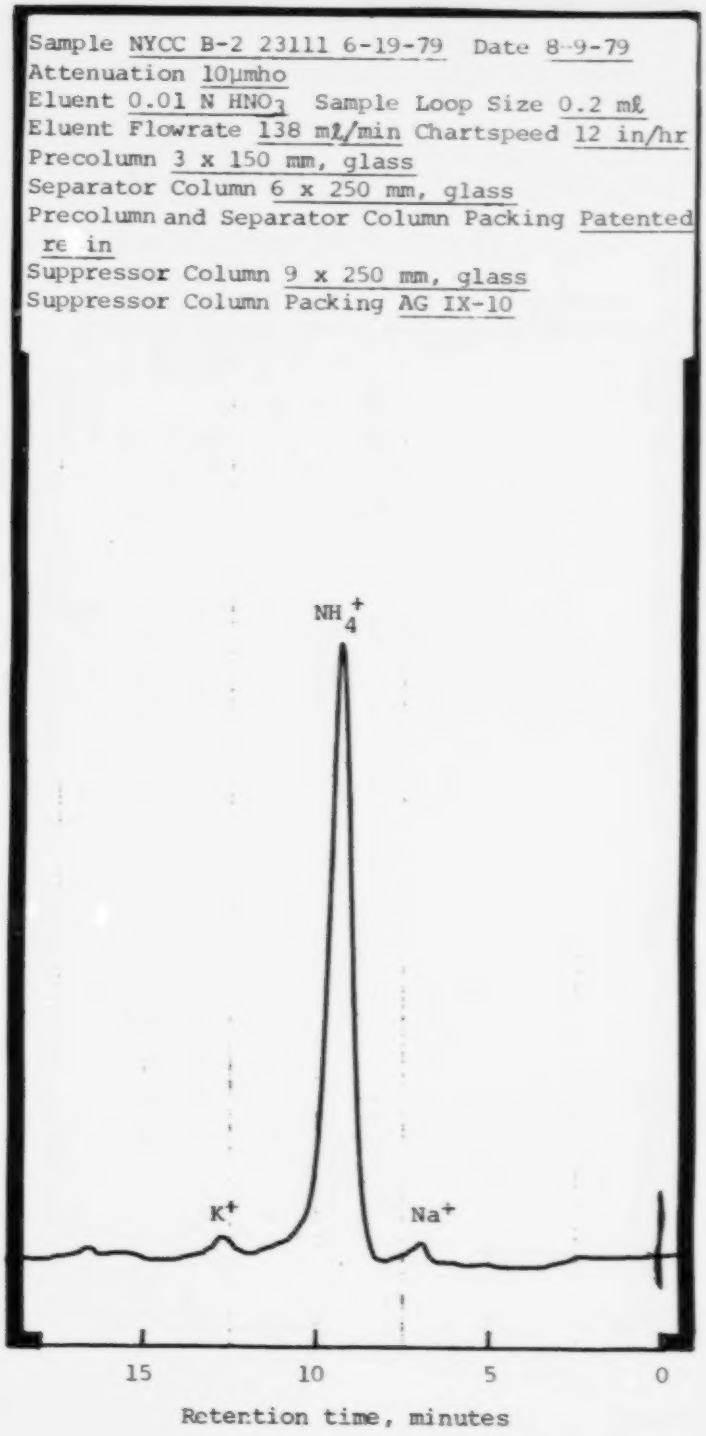
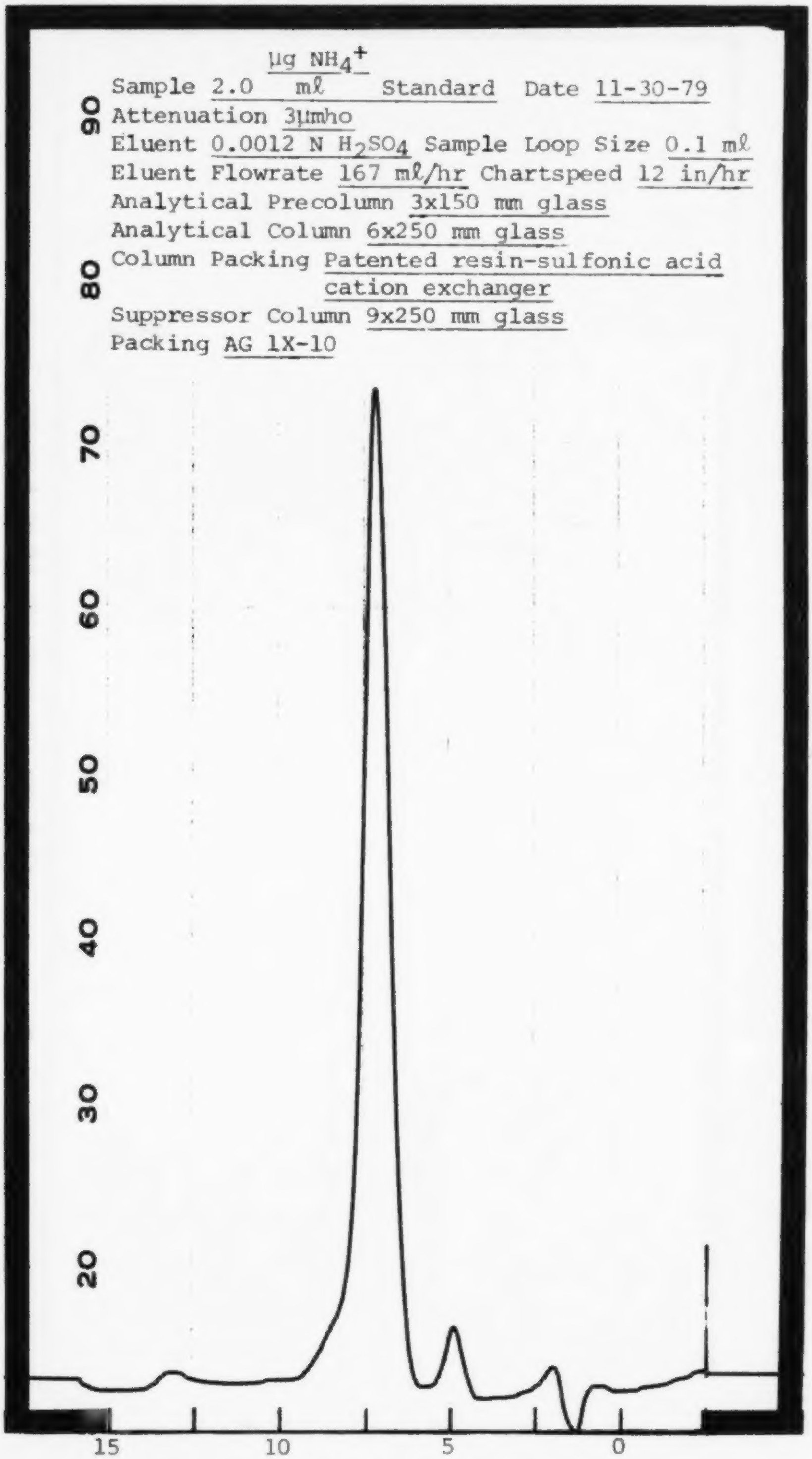

CVS
Glass
Impinger
Unused Sample
Saved as
Needed
Sample Analysis
in Ion Chromatograph
with Conductivity Cell
A/D
Converter
Recorder
Hewlett-Packard
3354
Computer System

Figure 4. NH_3 analysis flow schematic.



Sample NYCC B-2 23111 6-19-79 Date 8-9-79
Attenuation 10μmho
Eluent 0.01 N HNO_3 Sample Loop Size 0.2 mℓ
Eluent Flowrate 138 mℓ/min Chartspeed 12 in/hr
Precolumn 3 x 150 mm, glass
Separator Column 6 x 250 mm, glass
Precolumn and Separator Column Packing Patented resin
Suppressor Column 9 x 250 mm, glass
Suppressor Column Packing AG IX-10

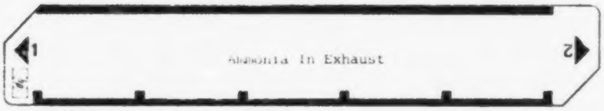
Figure 5. Sample chromatogram.



Sample 2.0 $\frac{\mu g\ NH_4^+}{m\ell}$ Standard Date 11-30-79
Attenuation 3µmho
Eluent 0.0012 N H_2SO_4 Sample Loop Size 0.1 mℓ
Eluent Flowrate 167 mℓ/hr Chartspeed 12 in/hr
Analytical Precolumn 3x150 mm glass
Analytical Column 6x250 mm glass
Column Packing Patented resin-sulfonic acid cation exchanger
Suppressor Column 9x250 mm glass
Packing AG 1X-10

Figure 6. Standard chromatogram

User Instructions



STEP	INSTRUCTIONS	INPUT DATA UNITS	KEYS		OUTPUT DATA UNITS
0_1	Switch to on; Switch to run				
0_2	Feed Card in from right to left				
0_3	Set Decimal place		4	[illegible]	
1	Input Sample Volume	ft^3	A		
2	Input Barometric Pressure	"Hg	R/S		
3	Input Sample Temperature	°F	R/S		
4	Input Dilution Factor		R/S		
5	Input Absorbing Reagent Volume	mℓ	R/S		
6	Input Standard Concentration	$\mu gNH_4^+/m\ell$	R/S		
7	Input Standard Area		R/S		
8	Input Sample Area		R/S		
9	Output Sample Concentration		R/S		$\mu gNH_3/m^3$
10	Output Sample Concentration				PPM
			h	RTN	

Figure 7. HP-67 user instructions.

STEP	KEY ENTRY	KEY CODE	COMMENTS	STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	Input Sample Vol, ft^3				
	3	03					
	5	05					
	.	83		060			
	3	03					
	1	01					
	÷	81					
	5	05					
	2	02					
010	8	08					
	X	71					
	2	02					
	9	09					
	.	83		070			
	9	09					
	2	02					
	÷	81					
	R/S	84	Input Barometer, "Hg				
	X	71					
020	STO 1	33 01					
	R/S	84	Input Sample Temp, °F				
	4	04					
	6	06					
	0	00		080			
	+	61					
	RCL 1	34 01					
	h X≷y	35 52					
	÷	81					
	h 1/X	35 62					
030	R/S	84	Input Dilution Factor				
	X	71					
	R/S	84	Input Abs Soln Vol, mℓ				
	X	71					
	R/S	84	Input Stand Conc, μg NH_4^+/mℓ	090			
	X	71					
	R/S	84	Input Stand Area				
	÷	81					
	R/S	84	Input Sample Area				
	X	71					
040	0	00					
	.	83					
	9	09					
	4	04					
	4	04		100			
	X	71					
	R/S	84	Output Conc, μg NH_3/m^3				
	0	00					
	.	83					
	0	00					
050	0	00					
	1	01					
	4	04					
	1	01					
	X	71		110			
	R/S	84					
	h RTN	35 22					

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A	B	C	D	E	I

Figure 7 (Cont'd). HP-67 program form.

This equation gives the concentration of NH_4^+ in the sample. To convert to $\frac{\mu g\ NH_3}{m\ell}$ the ratio of the formula weights of NH_3 to NH_4^+ is multiplied by C_{sa}.

$$C_{sa},\ \frac{\mu g\ NH_4^+}{m\ell} \times \frac{17.03\left(\frac{\mu g\ NH_3}{\mu\ mole}\right)}{18.04\left(\frac{\mu g\ NH_4^+}{\mu\ mole}\right)} = 0.944\ C_{sa}\left(\frac{\mu g\ NH_3}{m\ell}\right)$$

The next step involves the determination of the amount of NH_3 collected in the bubbler. This is obtained by multiplying the volume of absorbant (absorb. vol.) and a dilution factor (DF) by the concentration of ammonia collected.

$$0.944\ C_{sa}\left(\frac{\mu g\ NH_3}{m\ell}\right) \times \text{absorb. vol.}(m\ell) \times DF = \mu g\ NH_3$$

To find the concentration of NH_3 in exhaust the volume of gas collected is corrected to the specified temperature and pressure (68°F = 528°R and 29.92 "Hg). The volume as read from the digital readout in cubic feet is converted to cubic meters by dividing by 35.31 ft^3/m^3.

$$\frac{\text{VOL, } ft^3}{35.31\ \frac{ft^3}{m^3}} \times \frac{\text{B.P. "Hg}}{\text{29.92 "Hg}} \times \frac{528°R}{(\text{TEMP, °F} + 460)}$$

where VOL = volume of gas collected, ft^3

B.P. = collection pressure, "Hg

TEMP = collection temperature, °F

The concentration of NH_3 is then calculated by dividing $\mu g\ NH_3$ by the volume of gas.

$$\frac{0.944 \times \frac{C_{st}\left(\frac{\mu g\ NH_4^+}{m\ell}\right) \times PA_{sa}}{PA_{st}} \times \text{absorb. vol, } m\ell \times DF}{\frac{\text{VOL, } ft^3}{35.31\ \frac{ft^3}{m^3}} \times \frac{\text{B.P. "Hg}}{\text{29.92 "Hg}} \times \frac{528°R}{(\text{TEMP, °F} + 460)}}$$

$$= \frac{0.944 \times C_{st}\left(\frac{\mu g\ NH_4^+}{m\ell}\right) \times PA_{sa} \times \text{absorb. vol, } m\ell \times DF}{\text{VOL, } ft^3 \times PA_{st}} \times$$

$$\frac{35.31\ \frac{ft^3}{m^3} \times 29.92\ \text{"Hg}\quad (\text{TEMP, °F} + 460)}{\text{B.P., " Hg} \times 528\text{°R}}$$

$$= \frac{\mu g\ NH_3}{m^3}$$

The concentration of ammonia can also be expressed in ppm NH_3 by taking into consideration the density of the gas at the desired conditions (68°F, 29.92 "Hg). The fifth edition of the Matheson Gas Data Book lists the specific gravity of ammonia gas at 70°F and 1 atm pressure at 1.411 ℓ/g. The inverse of the specific gravity gives a density of 0.709 $\frac{g}{\ell}$. If the volume of 1ℓ of gas is corrected for temperature,

$$V = 1\ \ell \times \frac{528\text{°F}}{(70\text{°F} + 460)} = 0.996\ \ell,$$

it can be divided into the weight of the gas to give the density at 68°F.

$$\frac{0.709\ g}{0.996\ \ell} = 0.712\ \frac{g}{\ell} = 712\ \frac{\mu g}{m\ell}$$

$$= 0.00141\ \frac{m\ell}{\mu g\ NH_3}$$

When the inverse of density is multiplied by the concentration in $\frac{\mu g\ NH_3}{m^3}$, the concentration is given in ppm NH_3.

$$\frac{\mu g\ NH_3}{m^3} \times 0.00141\ \frac{m\ell}{\mu g\ NH_3} = \frac{m\ell}{m^3} = \text{ppm } NH_3$$

Sample Calculation

The two examples will be calculated from information recorded on the data sheet (Figure 8). This information does not necessarily represent actual experimental data but serves as a means of confirming calculations done by hand with those done with the Hewlett-Packard Calculator.

Example 1

Assume that in the FTP-2 driving cycle that 2.652 ft^3 of dilute exhaust is collected in 25 mℓ of 0.01 N H_2SO_4 at 74.2°F and 29.42 "Hg. When the undiluted sample is injected into the Ion Chromatograph it yields a peak area of 3800 counts. A 9 $\frac{\mu g\ NH_4^+}{m\ell}$ standard similarly injected produces an area of 4800 counts.

SwRI Project No. ____________ Test No. _____ Test Date: _____________ Vehicle: _____________
Fuel: ______________ CVS No. _____ Tunnel Size ________ Driver: ____________ Miles: _______
Sample Collection By: _______ Chemical Analysis By: ______________ Calculations By: _______
General Comments: ____

Driving Cycle	Sampling Conditions			Dilution Factor	Absorb. Reagent Volume mℓ	Standard		Sample		
	Volume Ft^3	B.P. "Hg	Temp. °F			$\mu g NH_4^+/m\ell$	Area	Area	$\mu g NH_3/m^3$	ppm
FTP-1	1.546	29.40	74.0	1	25	4	3500	2500	1590	2.23
FTP-2	2.652	29.42	74.2	1	25	9	4800	3800	2300	3.25
FTP-3	1.625	29.44	74.5	1	25	5	3600	2700	1980	2.79
SET-7	4.212	29.45	74.3	1	25	15	4500	3500	2370	3.35
HFET	2.197	29.47	74.7	1	25	9	5000	3500	2460	3.46
NYCC	1.890	29.49	74.7	1	25	8	5200	3500	2440	3.44
BG	2.600	29.50	74.4	1	25	1.5	3300	2500	374	0.53
	1	2	3	4	5	6	7	8		

Figure 8. NH_3 Data Sheet.

The equation needed to calculate the concentration of ammonia follows:

$$\frac{\mu g\ NH_3}{m^3} = \frac{0.944 \times C_{st}\left(\frac{\mu g\ NH_4{}^+}{m\ell}\right) \times PA_{sa} \times \text{absorb. vol, } m\ell}{\text{VOL, } ft^3 \times PA_{st}} \times$$

$$\frac{DF \times 35.31\ ft^3/m^3 \times 29.92\ \text{"Hg} \times (\text{TEMP, } {}^\circ F + 460)}{\text{B.P., "Hg} \times 528^\circ R}$$

$$\frac{0.944 \times 9 \times 3800 \times 25 \times 1 \times 35.31 \times 29.92 \times (74.2 + 460)}{2.652 \times 4800 \times 20.42 \times 528}$$

$$= 2300\ \frac{\mu g\ NH_3}{m^3}$$

$$ppm\ NH_3 = 2300 \times 0.00141 = 3.25\ ppm\ NH_3$$

Example 2

Assume that 1.890 ft^3 of dilute automotive exhaust was collected in 25 mℓ of 0.01 N H_2SO_4 during the NYCC driving cycle. The sampling conditions during this test were 74.7°F and 29.49 "Hg. When the undiluted sample was injected into the ion chromatograph the peak produced had an area of 3500 counts. When an 8 $\frac{\mu g\ NH_4{}^+}{m\ell}$ standard was injected it produced an area of 5200 counts.

The same equations in Example one are used to give concentrations of NH_3 of 2440 $\frac{\mu g\ NH_3}{m^3}$ and 3.44 ppm NH_3.

EQUIPMENT

The equipment section lists the equipment used in the ammonia procedure. It is divided into four sections corresponding to each major division in the procedure: Sampling, Analysis, Water Filtration and Sample Preparation. For convenience the item, manufacturer, model number and any additional pertinent information are included.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.

2. Flowmeters, Brooks Instrument Division, Model 1555, R-2-15-C, sapphire ball, 0-5 lit/min range, graduated 0-15.

3. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.

4. Digital readout for dry gas meter.

5. Sample pump, Thomas, Model #106 CA18, 4 lit/min free flow capacity.

6. Drying tube, Analabs Inc., Catalog #HGC-146,6" long, 1/4" brass fittings.

7. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 3/16" ID.

8. Teflon solenoid valve, The Fluorocarbon Company, Model #DV2-144N CA1.

9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps and connectors, etc.

10. Miscellaneous electrical switches, lights, wiring, etc.

11. Regulating valve, Nupro 4MG, stainless steel.

12. Iron/Constantan type J, Thermo Sensors Corporation, single thermocouple, 1/4" OD stainless steel metal sheath.

13. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

14. 30 mℓ polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.

15. Modified 25 mm A-H microanalysis filter holder, Millipore, Catalog #XX50 020 00.

16. Fluoropore 25 mm filters, Millipore, Catalog #FHLP 025 00, 0.5 micron pore size.

17. Flexible heavy insulation heating tape, Briskeat®, width-1/2", length-48".

18. Temperature Controller, Athena, 100-600°F.

19. Heated TFE Teflon hose, Technical Heaters Inc., 5' x 1/4", temperature limit 400°F.

Analysis

1. Dionex Model 10 Ion Chromatograph.

2. Multivoltage recorder, Texas Instruments, Model #PS02W6A.

3. Polyethylene cubitainers, Cole Parmer Instrument Company, Catalog #6100-20, 1 gallon.

Water Filtration

1. Filtration apparatus, Millipore, Model #XX 1504700.

2. Filters, Millipore, Model #GSWP04700, 0.22 micron pore size.

Sample Preparation

1. 3 cc disposable syringes, Becton-Dickson, Model #5585.

2. 15 mℓ disposable polypropylene cups, Cole-Parmer Instrument Company, Catalog #6006-10.

3. Class A, 1 mℓ volumetric pipets.

4. Class A, 2 mℓ volumetric pipets.

5. Class A, 3 mℓ volumetric pipets.

6. Class A, 4 mℓ volumetric pipets.

7. Class A, 5 mℓ volumetric pipets.

8. Class A, 10 mℓ volumetric pipets.

9. Class A, 20 mℓ volumetric pipets.

10. Class A, 25 mℓ volumetric pipets.

11. Class A, 50 mℓ volumetric pipets.

12. Class A, 100 mℓ volumetric pipets.

13. Class A, 100 mℓ volumetric flasks.

14. Class A, 1000 mℓ volumetric flasks.

15. Class A, 2000 mℓ volumetric flasks.

16. Mohr pipet, 1 mℓ graduated 1/10.

LIST OF REAGENTS

The reagents used in the analysis of ammonia are presented in this section. In addition to the function of each reagent, the purity, manufacturer and catalog number are also listed.

1. Water-deionized and filtered through a 0.22 micron filter.

2. Standard
   Ammonia sulfate, $(NH_4)_2SO_4$, formula weight = 132.146, ACS analytical reagent grade, granular, J.T. Baker Chemical Co. #0792.

3. Absorbant
   Sulfuric acid, H_2SO_4, formula weight = 98.08, ACS analytical reagent grade, Mallinckrodt #2876.

4. Eluent
   Nitric Acid, HNO_3, formula weight = 63.01, ACS analytical reagent grade (Ultrex), J.T. Baker, #1-4801.

5. Regenerant
   Sodium hydroxide, NaOH, formula weight = 40.00, ACS analytical reagent grade, pellets, Mallinckrodt #7708.

PREPARATION OF REAGENTS

The water used in making all solutions and dilutions is prepared by filtering deionized water through a 0.22 micron filter. After filtration the water is stored in polyethylene bottles.

Standard($(NH_4)_2SO_4$)

The stock solution is prepared by diluting 0.3660 g of $(NH_4)_2SO_4$ to 1000 mℓ with water. This yields a solution with a concentration of 100 $\frac{\mu g\ NH_4^+}{m\ell}$. Less concentrated standards are made up by diluting portions of the stock solution to 100 mℓ with water using volumetric glassware.

Absorbing Solution (0.01 N H_2SO_4)

The absorbant is prepared by diluting 20.0 mℓ of the certified 1.000 N sulfuric acid to 2000 mℓ with water.

Eluent (0.0075 N HNO_3)*

A 1 N HNO_3 stock solution is prepared by diluting 62.5 mℓ of concentrated nitric acid to 1000 mℓ with water. The eluent is prepared by further diluting 15 mℓ of the stock solution to 2000 mℓ with water.

Regenerant (0.5 N NaOH)*

40.00g of NaOH is dissolved in water in a 2 liter volumetric flask and diluted to volume.

*4 liters of each of these solutions are prepared and stored in labeled polyethylene cubitainers.

REFERENCES

Braker, W. and Mossman, A.L., Matheson Gas Data Book, 5th Edition, East Rutherford, N.J., 1971, pg. 17.

Furman, N.H., (Ed.), Scott's Standard Methods of Chemical Analysis, 5th Edition, Van Nostrand, N.Y., 1958, Vol. 1, pg. 636.

Pifer, C.W. and Wollish, E.G., Anal. Chem. Vol. 24, pg. 519, 1952.

Kolthoff, I.M. and Stenger, V.A., Volumetric Analysis, Interscience, N.Y., 1947, Vol. 2, pg. 125.

Furman, N.H., (Ed.), Scott's Standard Methods of Chemical Analysis, 5th Edition, Van Nostrand, N.Y., 1958, Vol. 1, pg. 632.

Pierce, W.C., Haenisch, E.L., and Sawyer, D.T., Quantitative Analysis, Wiley, N.Y., 1958, pg. 260.

Kolthoff, I.M. and Stenger, V.A., Volumetric Analysis, Interscience, N.Y., 1954, Vol. 2, pg. 168.

Milner, O.I. and Zahner, R.J., Anal. Chem., Vol. 32, pg. 294, 1960.

Conway, E.J., Micro-Diffusion Analysis and Volumetric Error, 2nd Edition, Crosby-Lockwood, London, 1947.

Altman, C.J. G., de Heer, B.H.J., and Hermans, M.E.A., Anal. Chem., Vol. 35, pg. 596, 1963.

Vogel, A.I., Quantitative Inorganic Analysis, 3rd Edition, Longmans, Green, London, 1961, pg. 254.

Blinn, R.C. and Gunther, F.A., Anal. Chem., Vol. 29, pg.1882, 1957.

Kolthoff, I.M. and Stenger, V.A., Ind. Eng. Chem., Anal. Ed., Vol. 1, pg. 79, 1935.

Kolthoff, I.M. and Belcher, R., Volumetric Analysis, Interscience, N.Y., 1957, Vol. 3, pg. 582.

Welcher, F.J., Organic Analytical Reagents, Van Nostrand, N.Y., 1947, Vol. 1, pg. 376.

Rowe, D.J., Gas Journal, Vol. 265, pg. 49, 1951.

Burns, E.A., The Analysis of Exhaust Gases Trapped from Ablating Nozzles, TRW Report No. 9840-6001-TU 000, Redondo Beach, Cal., 1964.

Nyman, C.J. and Johnson, R.A., Anal. Chem., Vol. 29, pg. 483, 1957.

Norton, O.R. and Mann, C.K., Anal. Chem., Vol. 26, pg. 1180, 1954

Clear, A.J. and Roth, M., in Treatise on Analytical Chemistry, Kolthoff, I.M. and Elving, P.J. (Eds.), Interscience, N.Y., 1961, Part II, Vol. 5, pg. 284.

Kolthoff, I.M., Stricks, W., and Morren, L., Analyst, Vol. 78, pg. 405, 1953.

Laitinen, H.A. and Woerner, D.E., Anal. Chem., Vol. 27, pg. 215, 1955.

Arcand, G.M. and Swift, E.H., Anal. Chem., Vol. 28, pg. 440, 1956.

Krivis, A.F., Supp, G.R., and Gazda, E.S., Anal. Chem.,Vol. 35, pg. 2216, 1963.

De Ford, D.D., Johns, C.J., and Pitts, J.N., Anal. Chem., Vol. 23,pg. 941, 1951.

Segal N.S. and Woodley-Smith, R., Anal. Chem., Vol. 38, pg. 829, 1966.

Sambucetti, C.J., Anal. Chem., Vol. 38, pg. 105, 1966.

Barendrecht, E. and Janssen, N.G.L.M., Anal. Chem., Vol. 33, pg. 199, 1961.

Burns, E.A., Unpublished results, 1963.

Jenkins Jr., R.W., Cheek, C.H., and Linnenbom, V.S., Anal. Chem., Vol. 38, pg. 1257, 1966.

Miettinen, J.K., and Virtanen, A.I., Ann. Acad. Sci. Fennicae, ser. A. II., No. 41, 1951; through Chem. Abst. Vol. 46, pg. 11500, 1952.

Gilbert, T.R. and Clay, A.M., Anal. Chem., Vol. 45, pg. 1757, 1973.

Le Blanc, P.J. and Sliwinski, J.F., Am. Lab., Vol. 5, pg. 51, 1973.

Thomas, R.F. and Booth, R.L., Environ. Sci. Tech., Vol. 7, pg. 523, 1973.

Woodis Jr., T.C. and Cummings Jr., J.M., JAOAC, Vol. 56, pg.373, 1973.

Stockdale, D., Analyst, Vol. 84, pg. 667, 1959.

Sadek, F.S. and Reilley, C.N., Anal. Chem., Vol. 31, pg. 494, 1959.

Crane, F.E. and Smith, E.A., Chemist-Analyst, Vol. 49, pg. 38, 1960.

Crane, F.E. and Smith, E.A., Chemist-Analyst, Vol. 52, pg. 105, 1963.

Vogel, A.I., Quantitative Inorgrnic Analysis, 3rd Edition, Longmans, Green, London, 1969, pg. 566.

Furman, N.H., (Ed.), Scott's Standard Methods of Chemical Analysis, 5th Edition, Van Nostrand, N.Y., 1958, Vol. 1, pg. 2336.

Vogel, A.I., Quantitative Inorganic Analysis, 3rd Edition, Longmans, Green, London, 1961, pg. 1092.

Steyermark, A., Quantitative Organic Microanalysis, Blackstone, N.Y., 1951, pg. 56.

Taras, M.J., in Colorimetric Determination of Nonmetals, Boltz, D.F., (Ed.), Interscience, N.Y., 1958, pg. 84.

Miller, G.L. and Miller, E.E., Anal. Chem., Vol. 20, pg. 481, 1948.

Thompson, J.F. and Morrison, G.R., Anal. Chem., Vol. 23, pg. 1153, 1951.

Kruse, J.M. and Mellon, M.G., Anal. Chem., Vol. 25, pg. 1188, 1953.

Prochazkova, L., Anal. Chem., Vol. 36, pg. 865, 1964.

Scheurer, P.G. and Smith, F., Anal. Chem., Vol. 27, pg. 1616, 1955.

Bolleter, W.T., Bushman, C.J., and Tidwell, P.W., Anal. Chem., Vol. 33, pg. 592, 1961.

Zitomer, F. and Lambert, J.L., Anal. Chem., Vol. 34, pg. 1738, 1962.

Williams, D.D. and Miller, R.R., Anal. Chem., Vol. 34, pg. 225, 1962.

Howell, J.H. and Boltz, D.F., Anal. Chem., Vol. 36, pg. 1799, 1964.

Gunther, F.A., Barkley, J.H., Kolbezen, M.J., Blinn, R.C., and Staggs, E.A., Anal. Chem., Vol. 28, pg. 1985. 1956.

Kolbezen M.J., Eckert, J.W., and Wilson, C.W., Anal. Chem., Vol. 36, pg. 593, 1964.

Pierson, R.H., Fletcher, A.A., and St. Clair Gantz, E., Anal. Chem. Vol. 28, pg. 1218, 1956.

Vandeveene, L. and Oudewater, J., Centre Belge D'Etude et de Documentation des Eaux, Vol. 352, pg. 127, 1973.

Banwart, W.L., Tabatabai, M.A. and Bremner, J.M., Comm. Soil Sci. Plant Anal., Vol. 3, pg. 449, 1972.

Byrne, E. and Power, T., Comm. Soil Sci. Plant Anal., Vol. 5, pg. 51, 1974.

Mc William, D.J., and Ough, C.S., Amer. J. Enol. Viticult, Vol. 25, pg. 67, 1974.

Sigsby Jr., J.E., Black, F.M., Bellar, T.A., and Klosterman, D.L., Environ. Sci. Tech., Vol. 7, pg. 51, 1973.

Christian, G.D., Knoblock, E.C., Purdy, W.C., Anal. Chem., Vol. 35, pg. 2217, 1963.

Zweidinger, R.B., Tejeda, S.B., Sigsby Jr., J.B., and Bradow, R.L., "The Application of Ion Chormatography to the Analysis of Ammonia and Alkyl Amines in Automotive Exhaust," Symposium on Ion Chromatographic Analysis of Environmental Pollutants, EPA, Research Triangle Park, N.C., April 1977.

APPENDIX I

ORGANIC SULFIDES PROCEDURE

THE MEASUREMENT OF ORGANIC SULFIDES IN EXHAUST

The measurement of organic sulfides; carbonyl sulfide (COS), methyl sulfide (dimethylsulfide, $(CH_3)_2S$), ethyl sulfide (diethylsulfide, $(C_2H_5)_2S$) and methyl disulfide (dimethyldisulfide, $(CH_3)_2S_2$) in exhaust is accomplished by passing the exhaust through Tenax GC traps at -76°C. The organic sulfides are removed from the exhaust by the traps at this temperature. The exhaust sample is collected continuously during the test cycle. The organic sulfides are thermally desorbed from the traps into a gas chromatograph sampling system and injected into a gas chromatograph equipped with a flame photometric detector for analysis. External organic sulfide standards generated from permeation tubes are used to quantify the results. Detection limits are on the order of 0.1 ppb.

SAMPLING SYSTEM

A Tenax GC trap is used to collect exhaust samples for the analysis of the organic sulfides. A flow schematic of the sample collection system is shown in Figure 1. The trap collects 99+ percent of the sulfides at flows up to 130 mℓ/min. Several views of the sampling system are shown in Figure 2. The various components of the sampling system and their functions are listed below.

Item	Component	Description
1	$NaHCO_3$ trap	2" × 3/8" OD × 0.035" wall stainless steel cartridge packed with 5 percent $NaHCO_3$ on 45/60 mesh Chromosorb P (this trap removes SO_2 from the exhaust sample).
2	Tenax-GC trap	2" × 3/8" OD × 0.035" wall stainless steel cartridge packed with preconditioned 60/80 mesh Tenax-GC (this trap collects and concentrates the organic sulfides).
3	Perma-Pure Drier	Model PD-62512S Perma-Pure Drier (this dryer removes the moisture in the exhaust without jeopardizing the sample integrity).
4	Sample Pump	Model MB-158 Metal Bellows Vacuum/Compressor Pump. The sample pump pulls the exhaust sample through flip-top filter and Perma-Pure Drier and forces the sample under pressure through the remainder of the system.

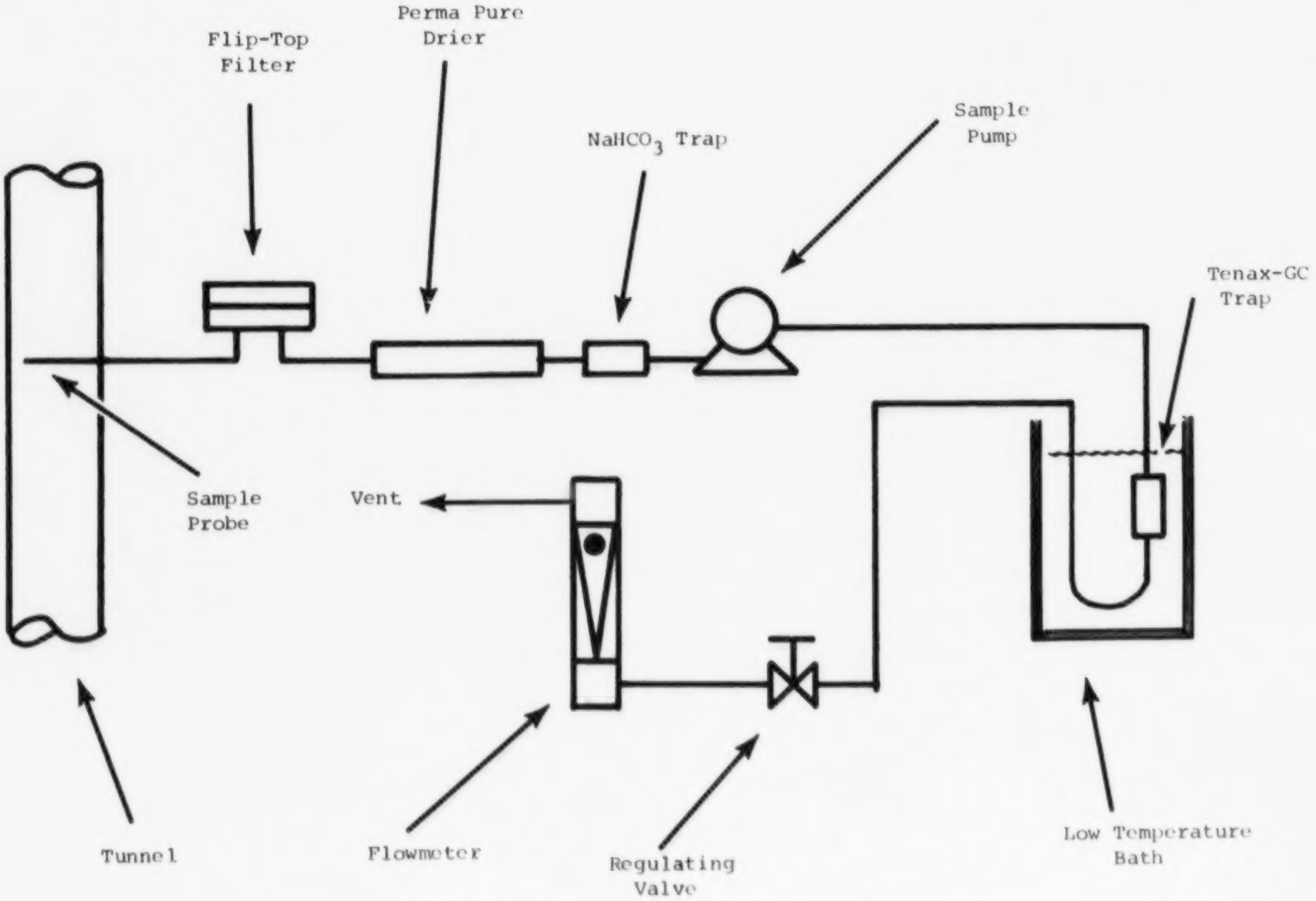
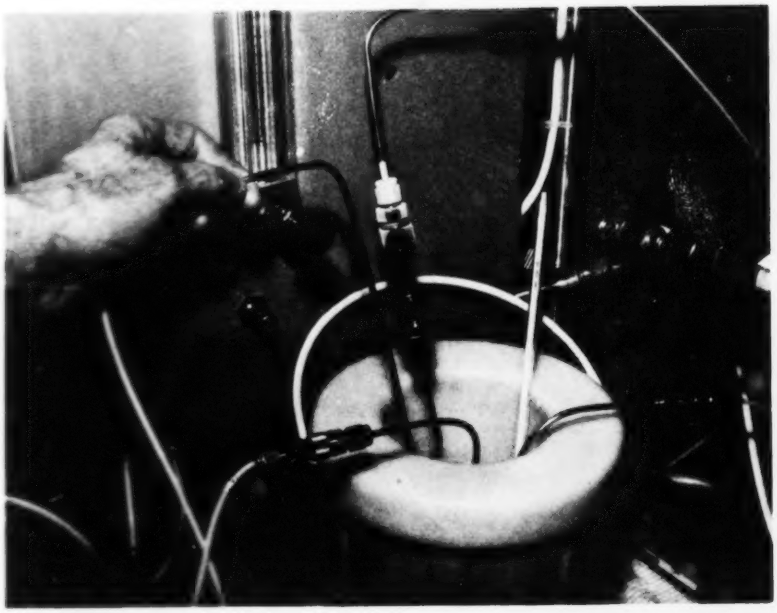

Flip-Top Filter
Perma Pure Drier
NaHCO$_3$ Trap
Sample Pump
Tenax-GC Trap
Sample Probe
Vent
Tunnel
Flowmeter
Regulating Valve
Low Temperature Bath

Figure 1. Organic sulfide sample flow schematic.



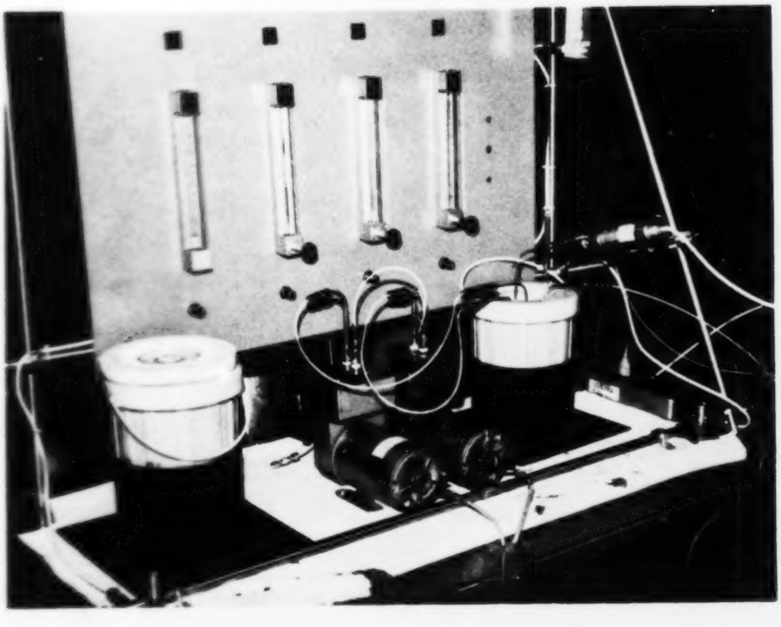
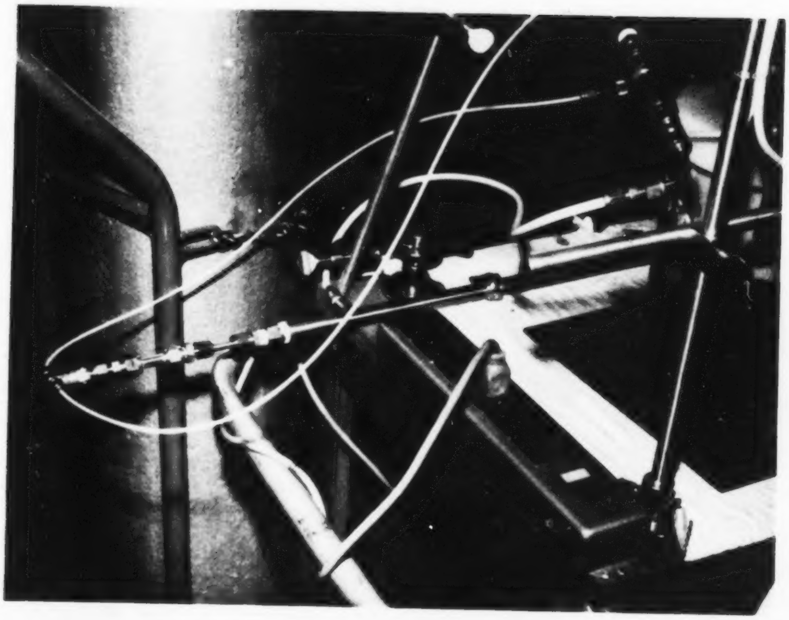


Figure 2. Several views of the organic sulfide sampling system.



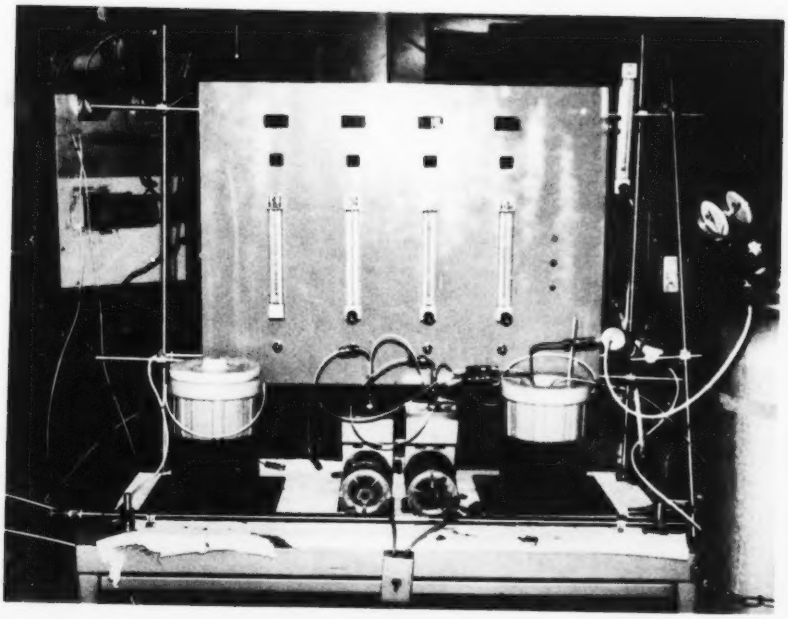


Figure 2 (Cont'd). Several views of the organic sulfide sampling system.

5	Low temp bath	A constant low temperature bath is obtained by using a CO_2-isopropyl alcohol slurry. A bath temperature of -76 to -78°C is obtained with this bath.
6	Flip-top filter	A 7.0 cm stainless steel flip-top filter is included to remove all particulate from the exhaust sample prior to its entry into the Perma-Pure Drier.
7	Regulating valve	A Nupro SS-4MG regulating needle valve is used to control the exhaust flow through the $NaHCO_3$ and Tenax-GC traps.
8	Flowmeter	A Brooks Model 1550 flowmeter with R-2-15-AAA (SS float) is used to determine the exhaust sampling rate.

TRAP PREPARATION

The Tenax traps used for the collection of the organic sulfides are prepared by filling a 2" × 3/8" OD (0.028" wall) stainless steel tube with approximately 1 gram of 60/80 mesh Tenax-GC. Stainless steel fritted discs, 50µ, 3/8" OD are placed at each end of the trap to hold the Tenax in the trap while allowing a gas flow through the trap. Nut and ferrules, 3/8", and Swagelok 3/8" × 1/8" stainless steel reducing unions hold the fritted discs in place and allow the trap to be inserted into the sampling system. A 1/8" stainless steel cap is placed on each end to prevent moisture and other unwanted compounds from collecting in the trap. Figure 3 shows a view of the completed trap and of its components. When a trap is ready to use, 1/8" Swagelok nuts and ferrules are used to connect 1/8" stainless steel tubing to each end of the trap. At the other end of each piece of the 1/8" stainless steel tubing a miniature male quick connect is added with 1/8" Swagelok nuts and ferrules (Figure 4). The trap can now be connected by the miniature quick connects to the sampling system or the desorbing system with ease.

ORGANIC SULFIDE TENAX-GC TRAP CONDITIONING PROCEDURE

The analysis of organic sulfides in dilute automotive exhaust requires Tenax-GC traps that have been properly conditioned. It is absolutely essential that each Tenax-GC trap undergo the identical conditioning. This will insure that there are no residual compounds in the trap from a previous sample, or in the case of a fresh trap, to remove any residual solvents. Accurate quantitative data is directly dependent on performing the conditioning procedure in a consistent manner according to the procedure outlined in this section.

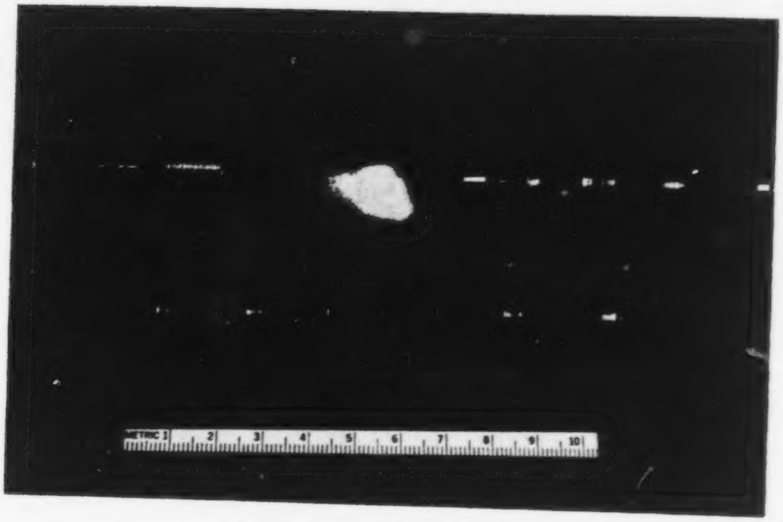

METRIC 1
2
3
4
5
6
7
8
9
10

Figure 3. Tenax-GC trap

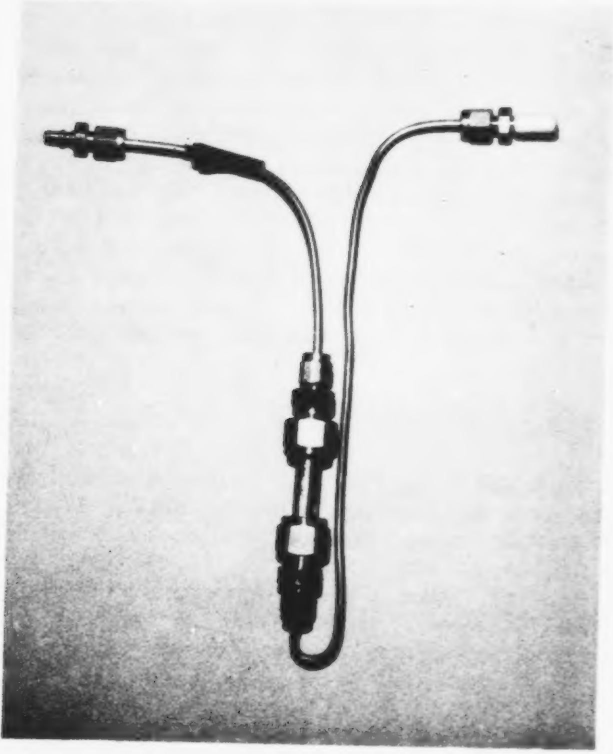


Figure 4. Tenax-GC trap with quick connect.

The Tenax-GC traps can be used repeatedly provided they are properly conditioned. Conditioning of the Tenax-GC traps is accomplished by purging with zero nitrogen at a selected temperature for a specified time period at a given flow rate. A system was developed that was capable of conditioning two Tenax-GC traps simultaneously. A flow schematic of this system is illustrated in Figure 5. Several views of the Tenax-GC sample conditioning system are presented in Figure 6. This system has been shown to reproducibly condition Tenax-GC traps to a negligible level of organic sulfides.

The organic sulfide trap conditioning procedure is listed below in a step-wise sequence.

1. Turn on the furnace and adjust the temperature to 325°C ± 25°C. The furnace should be allowed to stabilize for at least 15 minutes before the first trap is conditioned. The temperature readout on the furnace should be verified at least once a week with a digital thermocouple.

2. Connect the traps according to the flow schematic. Insert the traps into the furnace (with no nitrogen) and allow the traps to equilibriate for 5 minutes.

3. Turn on the nitrogen and adjust the flow to 500 mℓ/min.

4. After the 60-minute conditioning period, the trap is removed from the furnace and is allowed to cool to room temperature with nitrogen flowing through the trap.

5. After the trap returns to room temperature, turn off the nitrogen and remove the trap. The system is then ready for conditioning the next two traps.

NOTE 1: A master log should be maintained on the conditioning of each trap. It is the responsibility of the individual who is conditioning the traps to keep a record of all traps that have been conditioned, who conditioned them and the date that they were conditioned. All traps should be permanently identified to enable keeping of these records.

NOTE 2: Tenax-GC traps should not be placed in the furnace if the temperature is in excess of 375°C. This is the manufacturer's maximum recommended temperature and should not be exceeded. If this is allowed to happen, the chemical and physical properties of the Tenax-GC may be altered thereby affecting the trapping characteristics of the Tenax-GC.

ANALYTICAL PROCEDURE

The analysis of the organic sulfides (carbonyl sulfide, methyl sulfide, ehtyl sufide, and methyl disulfide) in dilute exhaust is accomplished by collecting the organic sulfides in Tenax traps at -76°C. The organic sulfides

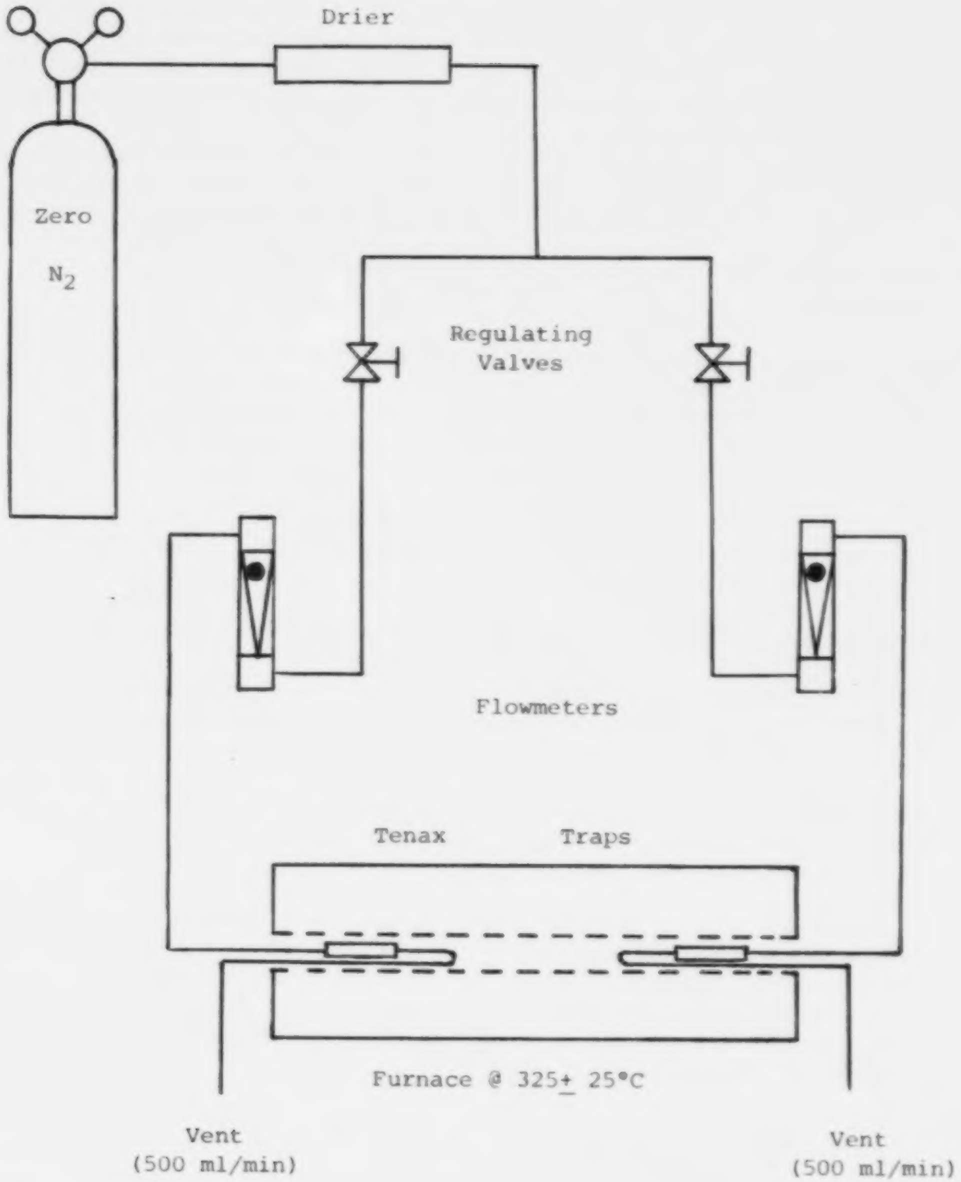

Drier
Zero
N_2
Regulating Valves
Flowmeters
Tenax Traps
Furnace @ 325± 25°C
Vent (500 ml/min)
Vent (500 ml/min)

Figure 5. Flow schematic for conditioning Tenax-GC traps for organic sulfide analysis (dual system).

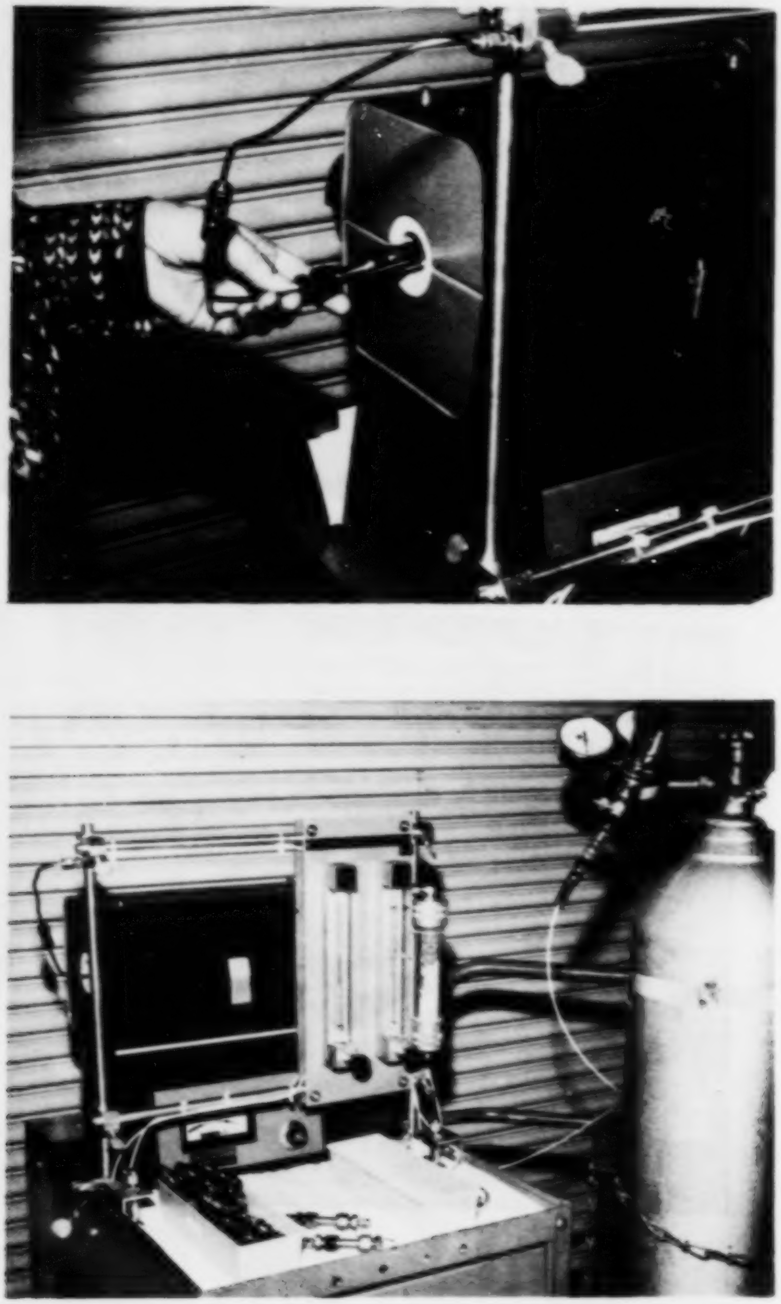
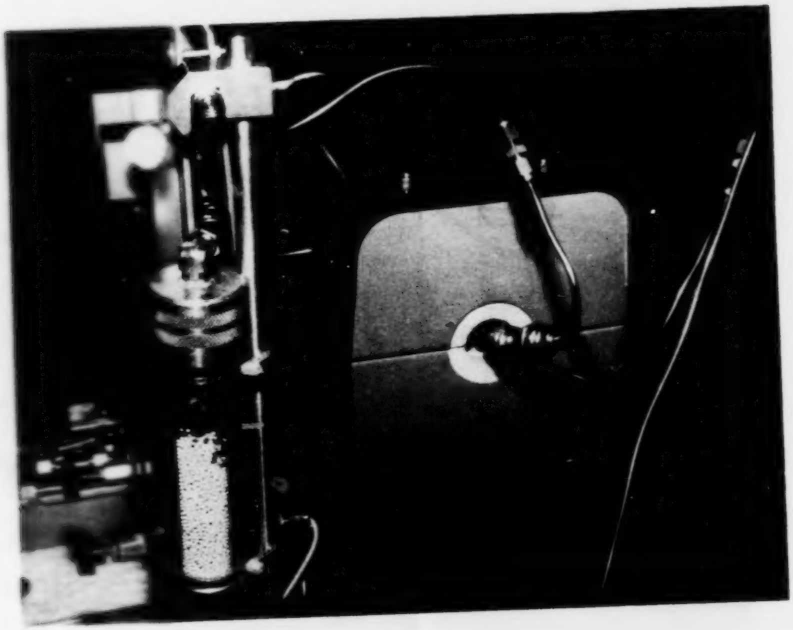


Figure 6. Several views of Tenax-GC trap conditioning system.



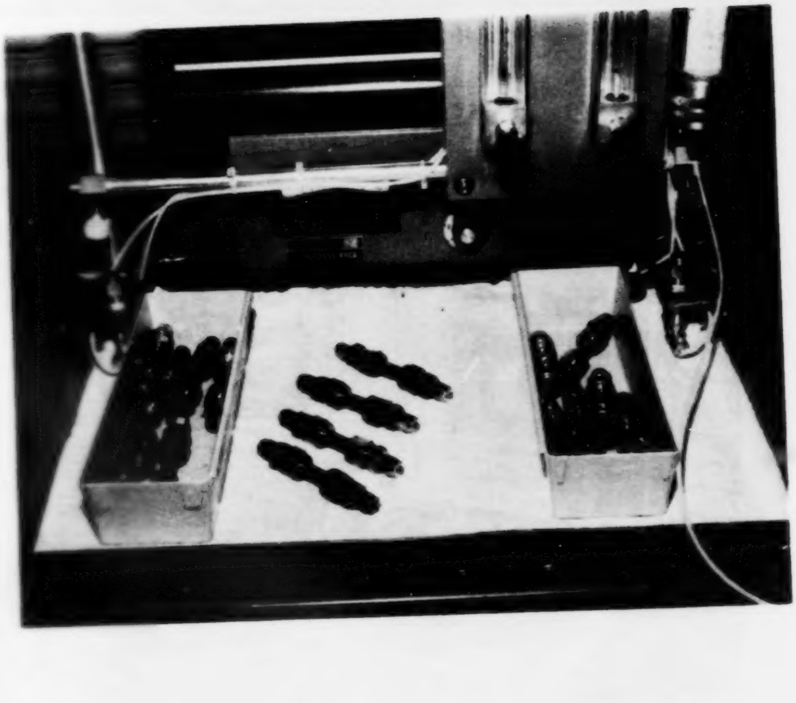


Figure 6 (Cont'd). Several views of Tenax-GC trap conditioning system.

are thermally desorbed from the trap into a gas chromatograph sampling system. The organic sulfides are analyzed by injecting the desorbed sample into a gas chromatograph equipped with a flame photometric detector. A standard blend containing known amounts of the four organic sulfides is injected into the gas chromatograph to quantify the results. From the GC analysis of the sample, the analysis of the standard blend, and the measured volume of exhaust sampled, the concentration of the organic sulfides in the exhaust can be determined. The analysis flow schematic for the organic sulfides is shown in Figure 7. A detailed description of the procedure follows.

The organic sulfides are removed from the exhaust stream by trapping them in Tenax GC traps. A sample pump pulls dilute exhaust from CVS through a flip-top filter, to remove particulate from the exhaust sample, and then through a Perma Pure Drier which selectively removes moisture from the exhaust sample. The moisture must be removed to prevent ice from forming in the Tenax traps. The ice formation would plug the trap and prevent the exhaust sample from passing through the trap. After exiting the Perma Pure Drier, the exhaust sample passes through a sodium bicarbonate trap which removes any interfering SO_2 in the exhaust sample. The exhaust sample is then pulled through the Tenax GC trap which removes the organic sulfides from the exhaust. The trap is held at -76°C with a dry ice-isopropyl alcohol slurry. After the organic sulfides have been removed by the Tenax trap, the exhaust passes through the sample pump, a regulating valve and a flow meter before exiting the sample system. The needle valve regulates the flow through the system which is monitored by the flow meter. A constant flow of 130 mℓ/min is maintained throughout the test. The Tenax trap is disconnected from the sampling system at the two miniature quick-connects and the two male miniature quick-connects are capped. The trap remains in the -76°C dry ice-isopropyl slurry until it is desorbed by the gas chromatograph injection system.

The Tenax trap is removed from the dry ice-isopropyl slurry, the liquid is quickly wiped from the trap, the the caps are removed from the ends of the trap. The trap is connected into the gas injection system with the two quick connects, (Figure 8) and the sample is immediately injected and placed into the Lindberg furnace operating at 300°C (Figure 9). The carrier gas upon injection flows through the loop carrying the contents into the gas chromatograph where the sulfides are separated and identified by their retention times. After the peaks of interest have passed through the column in the gas chromatograph, the system is backflushed to remove any high molecular weight impurities that could interfere with later analysis (Figure 10).

The gas chromatograph system used to analyze the organic sulfide sample is shown in Figure 11. The system consists of a Perkin-Elmer 3920B GC, and A/D converter and a recorder. The figure also shows the control system, the Lindberg furnace, and the Bendix valve oven. The GC is equipped with a linearized flame photometric detector which has a high sensitivity to sulfur containing compounds. The column consists of 6' × 1/8" Teflon tubing packed with 60/80 mesh Tenax GC. The carrier gas is helium which flows through the column at 30 mℓ/min. The optimum hydrogen and air flows are 40 mℓ/min and 360 mℓ/min, respectively. The column temperature, after injection of the sample, is programmed from 30°C to 140°C at 8° a minute. In a chromatogram

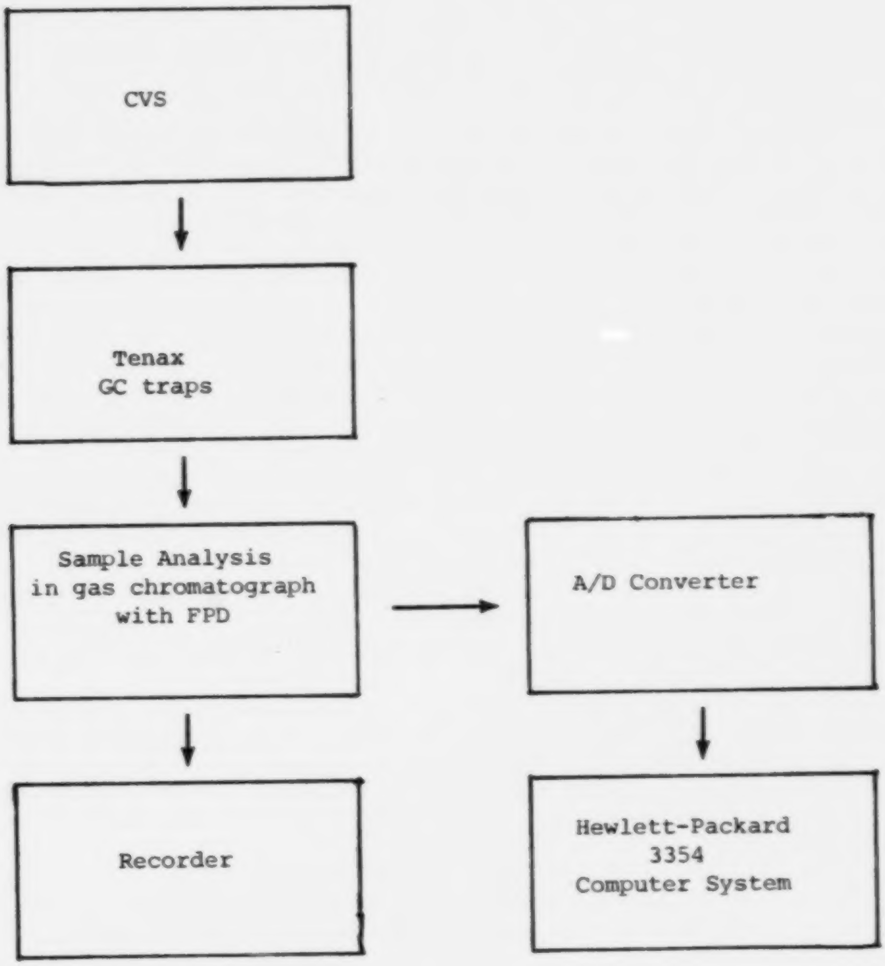

CVS
Tenax GC traps
Sample Analysis in gas chromatograph with FPD
A/D Converter
Recorder
Hewlett-Packard 3354 Computer System

Figure 7. Organic sulfide analysis flow schematic.

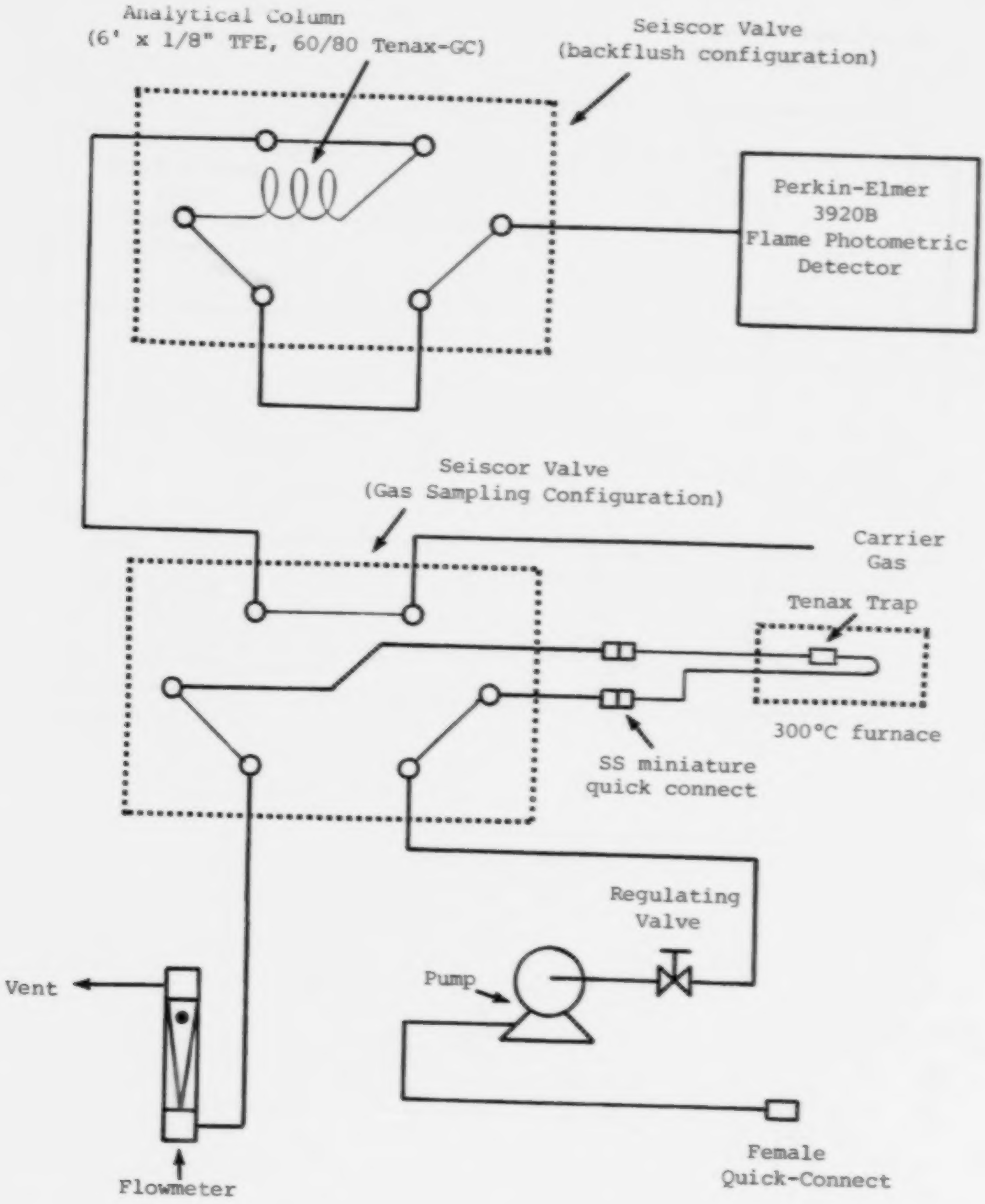

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax-GC)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920B
Flame Photometric
Detector
Seiscor Valve
(Gas Sampling Configuration)
Carrier
Gas
Tenax Trap
300°C furnace
SS miniature
quick connect
Regulating
Valve
Pump
Vent
Flowmeter
Female
Quick-Connect

Figure 8 . Flow schematic of organic sulfide analysis system (Step 1 - connect Tenax trap in GSV).

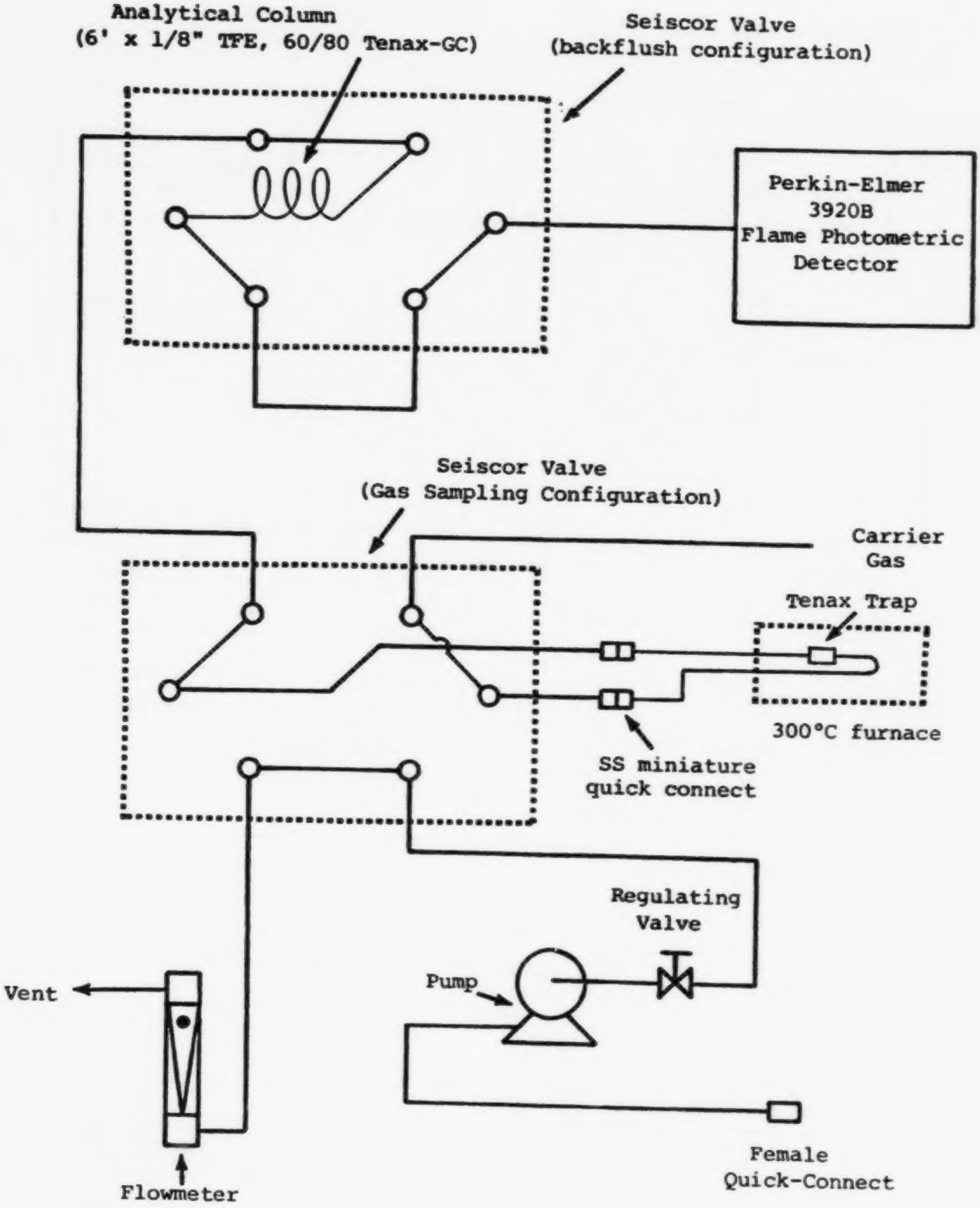

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax-GC)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920B
Flame Photometric
Detector
Seiscor Valve
(Gas Sampling Configuration)
Carrier
Gas
Tenax Trap
300°C furnace
SS miniature
quick connect
Regulating
Valve
Pump
Vent
Flowmeter
Female
Quick-Connect

Figure 9. Flow schematic of organic sulfide analysis system (Step 2 - inject Tenax trap contents into GC system).

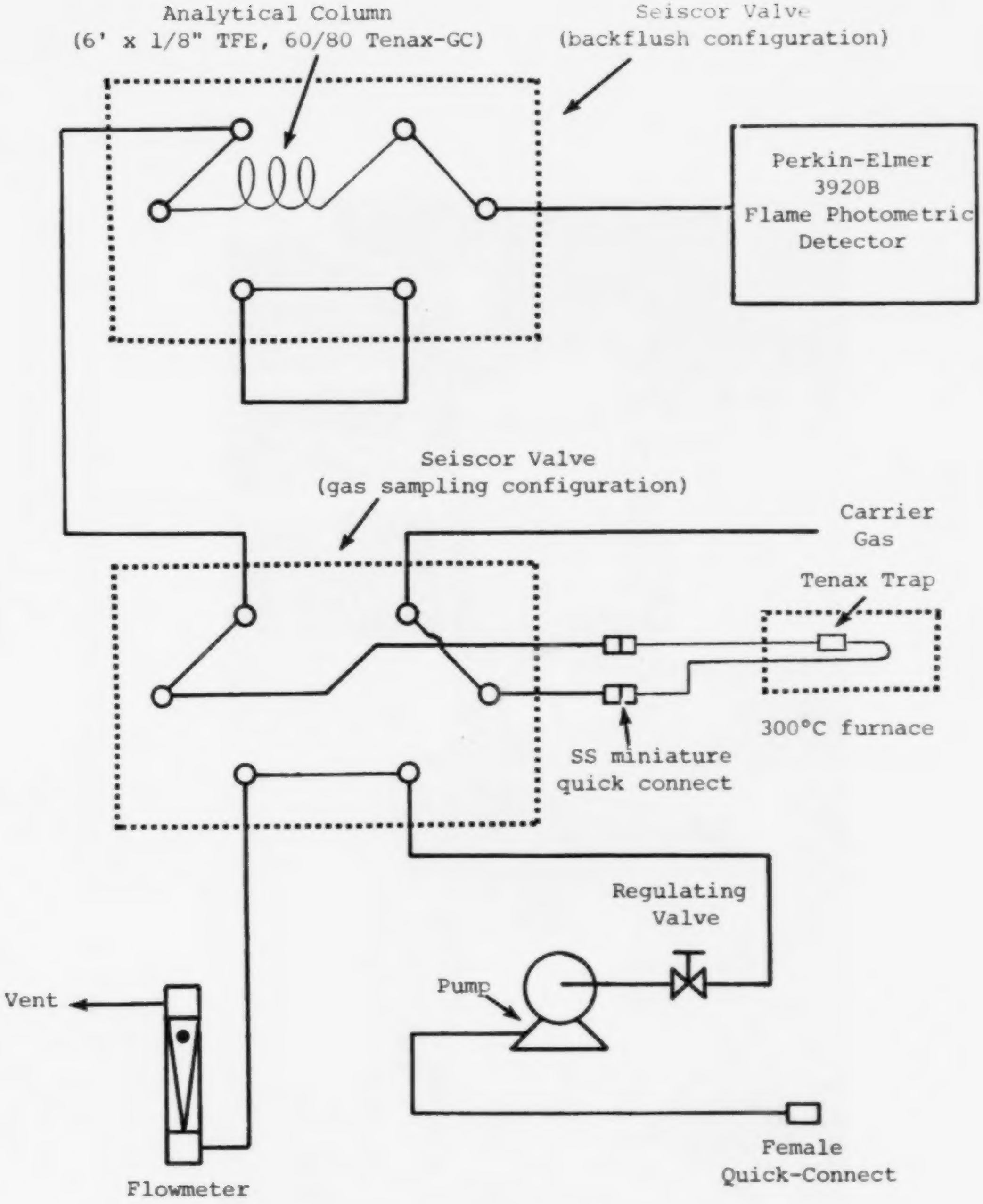

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax-GC)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920B
Flame Photometric
Detector
Seiscor Valve
(gas sampling configuration)
Carrier
Gas
Tenax Trap
300°C furnace
SS miniature
quick connect
Regulating
Valve
Pump
Vent
Flowmeter
Female
Quick-Connect

Figure 10. Flow schematic of organic sulfide analysis system (Step 3 - backflush analytical column).

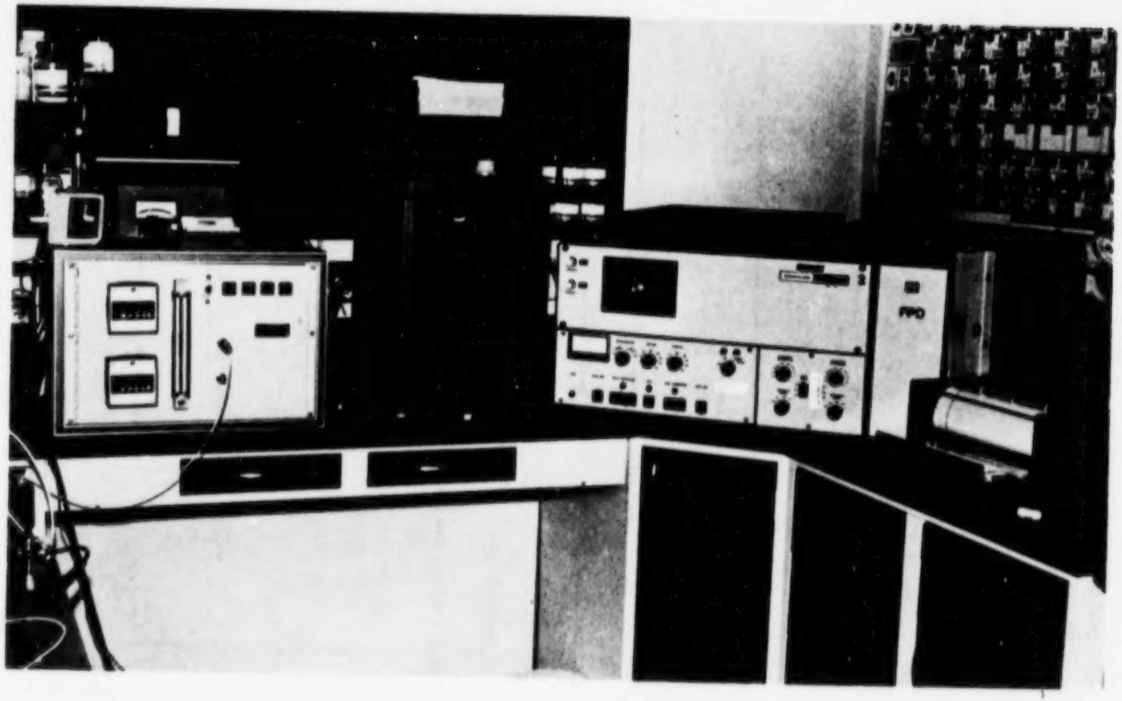


Figure 11. Organic sulfide analytical system.

of a standard sample (Figure 12) containing the four sulfides, the first peak eluted is carbonyl sulfide, followed by methyl sulfide, ethyl sulfide and methyl disulfide. The GC sulfide peaks are recorded on a Soltec dual channel recorder (1 mv) and peak areas and retention times are obtained from the Hewlett Packard GC computer system. A Metronix Dynacalibrator operating at 40°C and containing permeation tubes of carbonyl sulfide, methyl sulfide, ethyl sulfide, and methyl disulfide is used to supply standard concentrations of the organic sulfides. The permeation rate of each tube is monitored by monthly weighings. Zero nitrogen is used to dilute the permeation gases to the concentrations desired. The 10 mℓ sample loop is purged with this permeation gas for 10 minutes (Figure 13) and the 10 mℓ of permeation gas is then injected into the GC and analyzed (Figure 14). From the standard peak areas, the exhaust sample peak areas and the volume of exhaust sampled, the concentration of the organic sulfides in exhaust can be determined.

CONTROL SYSTEM

A control system was developed to systematically control the flow of the two Seiscor valves. This control is accomplished by ATC electric timers and ASCO electric solenoid valves. This system employs one Seiscor valve in a gas sampling valve (GSV) configuration with the second Seiscor valve in a backflush configuration. These valves are pneumatically operated and electrically controlled. The electrical schematic for the control of the Seiscor valves using the ATC timers and ASCO electric solenoid valves is shown in Figure 15. The flow schematic for vacuum and pressure lines to the Seiscor valve are presented in Figures 8-10 and 13-14. The Seiscor valves have been found to operate much more dependably if a vacuum assist is included in the valve actuation controls.

CALCULATIONS

This procedure has been developed to provide the user with the concentrations of the organic sulfides (carbonyl sulfide, methyl sulfide, ethyl sulfide, and methyl disulfide) in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm for each of the sulfides. The equations for determining the concentrations of $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to find the volume of exhaust sampled from the flow rate and the sampling time by the equation:

$$\text{Vol exp (m}\ell\text{)} = \text{F.R.}_{I}\ (\text{m}\ell/\text{min}) \times \text{Ti (sec)}/60\ \text{sec/min}$$

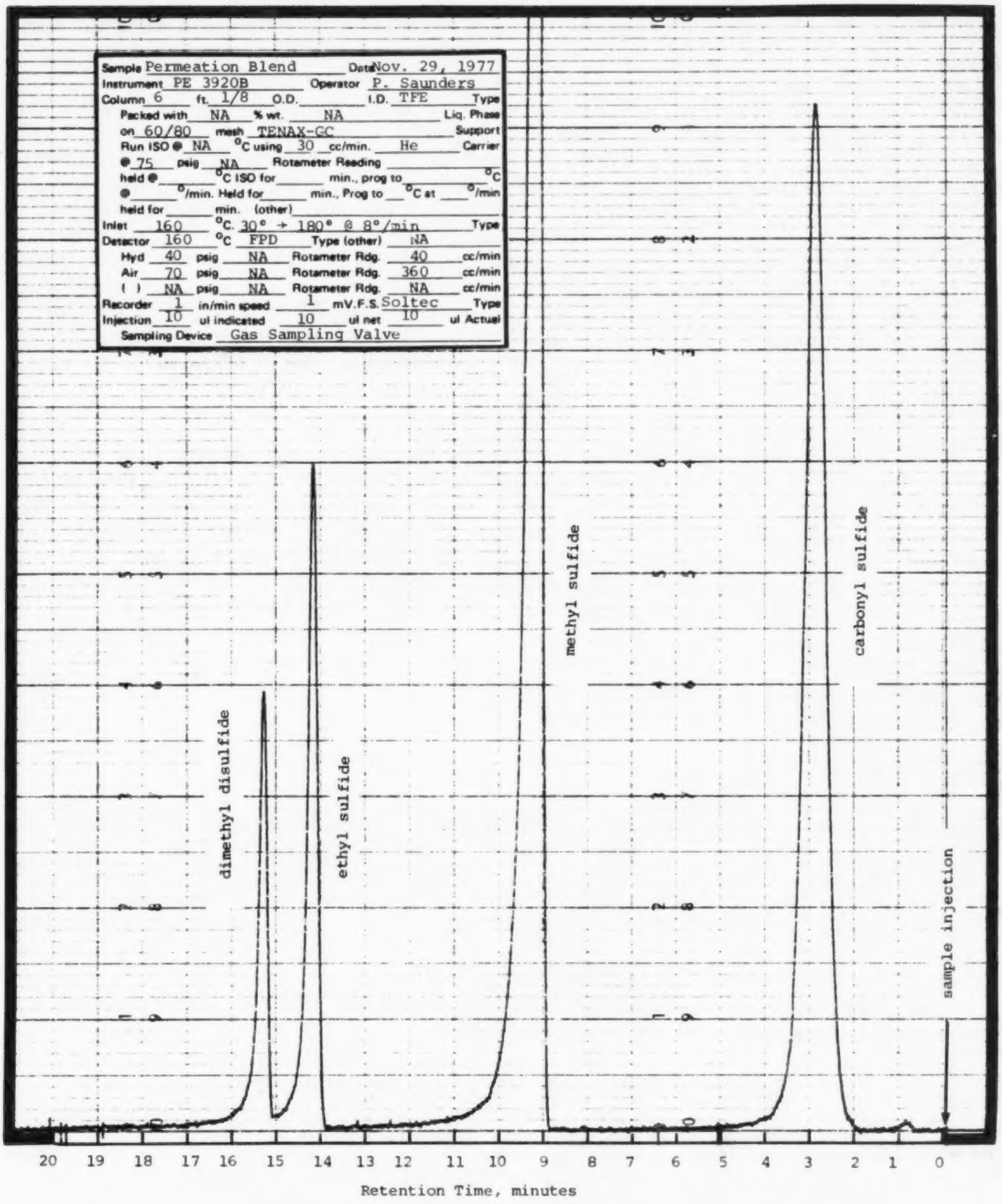
Vol exp (mℓ) = volume of gas sample in mℓ

F.R._{I} (mℓ/min) = flow rate of exhaust sample in mℓ/min

Ti (sec) = sampling time in minutes

60 sec/min = conversion of sample time in seconds to minutes

[Equation 1]



Sample Permeation Blend Date Nov. 29, 1977
Instrument PE 3920B Operator P. Saunders
Column 6 ft. 1/8 O.D. ____ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ NA °C using 30 cc/min. He Carrier
@ 75 psig NA Rotameter Reading ____
held @ ____ °C ISO for ____ min., prog to ____ °C
@ ____ °/min. Held for ____ min., Prog to ____ °C at ____ °/min
held for ____ min. (other) ____
Inlet 160 °C. 30° → 180° @ 8°/min Type
Detector 160 °C FPD Type (other) NA
Hyd 40 psig NA Rotameter Rdg. 40 cc/min
Air 70 psig NA Rotameter Rdg. 360 cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 in/min speed 1 mV.F.S. Soltec Type
Injection 10 ul indicated 10 ul net 10 ul Actual
Sampling Device Gas Sampling Valve

dimethyl disulfide
ethyl sulfide
methyl sulfide
carbonyl sulfide
sample injection
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
Retention Time, minutes

Figure 12. Chromatogram of organic sulfide standard.

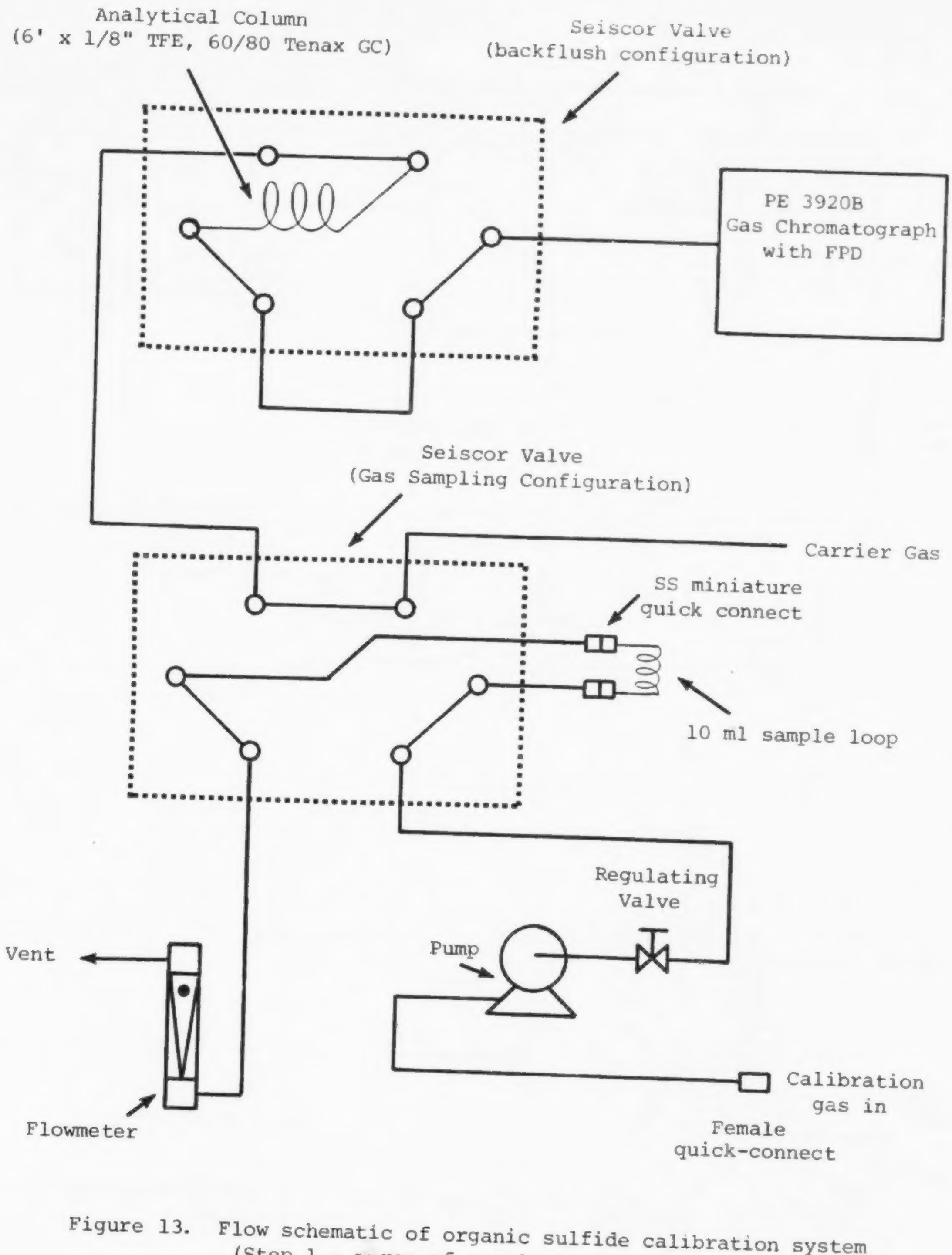

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax GC)
Seiscor Valve
(backflush configuration)
PE 3920B
Gas Chromatograph
with FPD
Seiscor Valve
(Gas Sampling Configuration)
Carrier Gas
SS miniature
quick connect
10 ml sample loop
Regulating
Valve
Pump
Vent
Flowmeter
Calibration
gas in
Female
quick-connect

Figure 13. Flow schematic of organic sulfide calibration system (Step 1 - purge of sample loop of GSV).

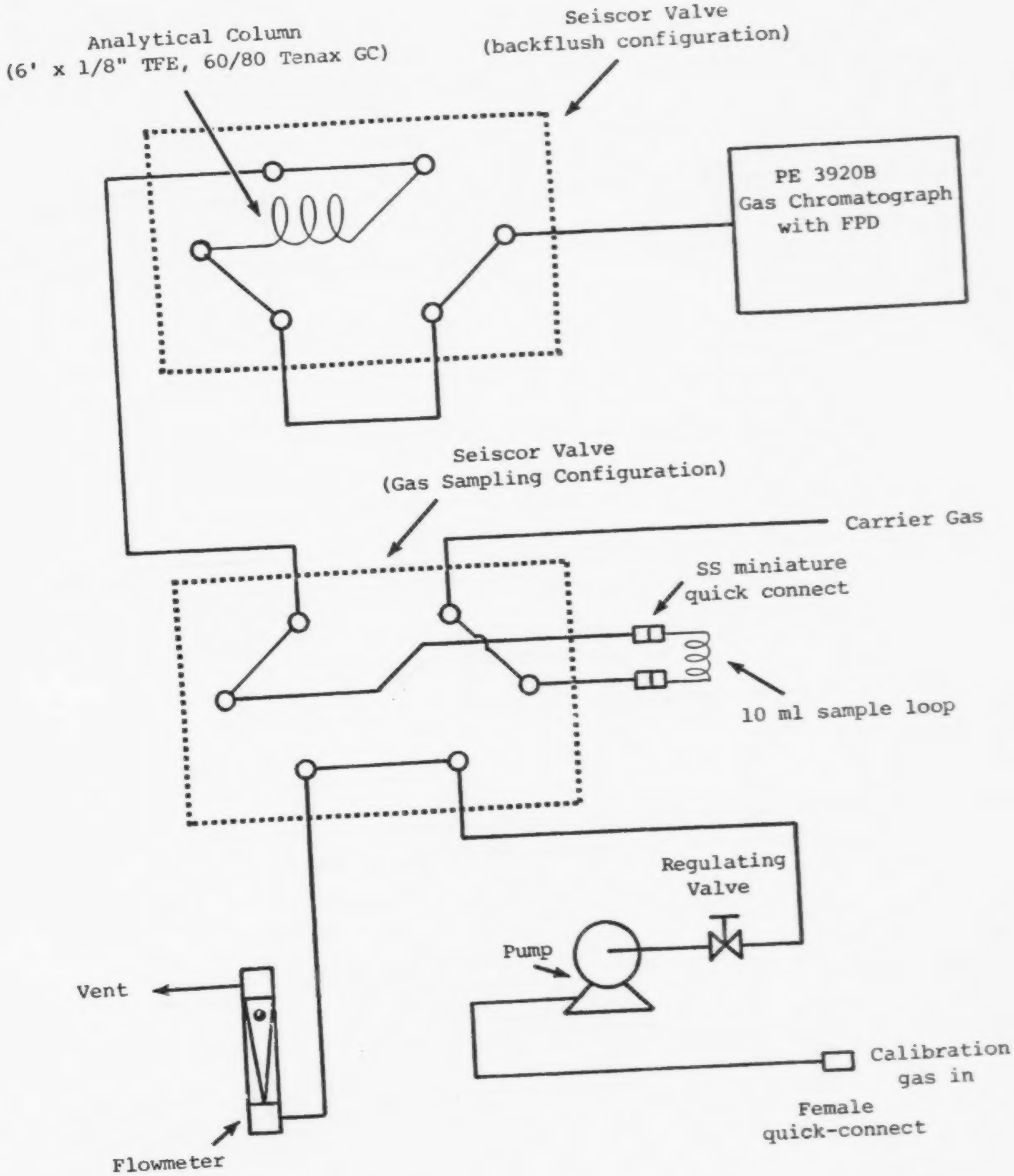

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax GC)
Seiscor Valve
(backflush configuration)
PE 3920B
Gas Chromatograph
with FPD
Seiscor Valve
(Gas Sampling Configuration)
Carrier Gas
SS miniature
quick connect
10 ml sample loop
Regulating
Valve
Pump
Vent
Calibration
gas in
Female
quick-connect
Flowmeter

Figure 14. Flow schematic of organic sulfide calibration system (Step 2 - inject calibration gas into GC system).

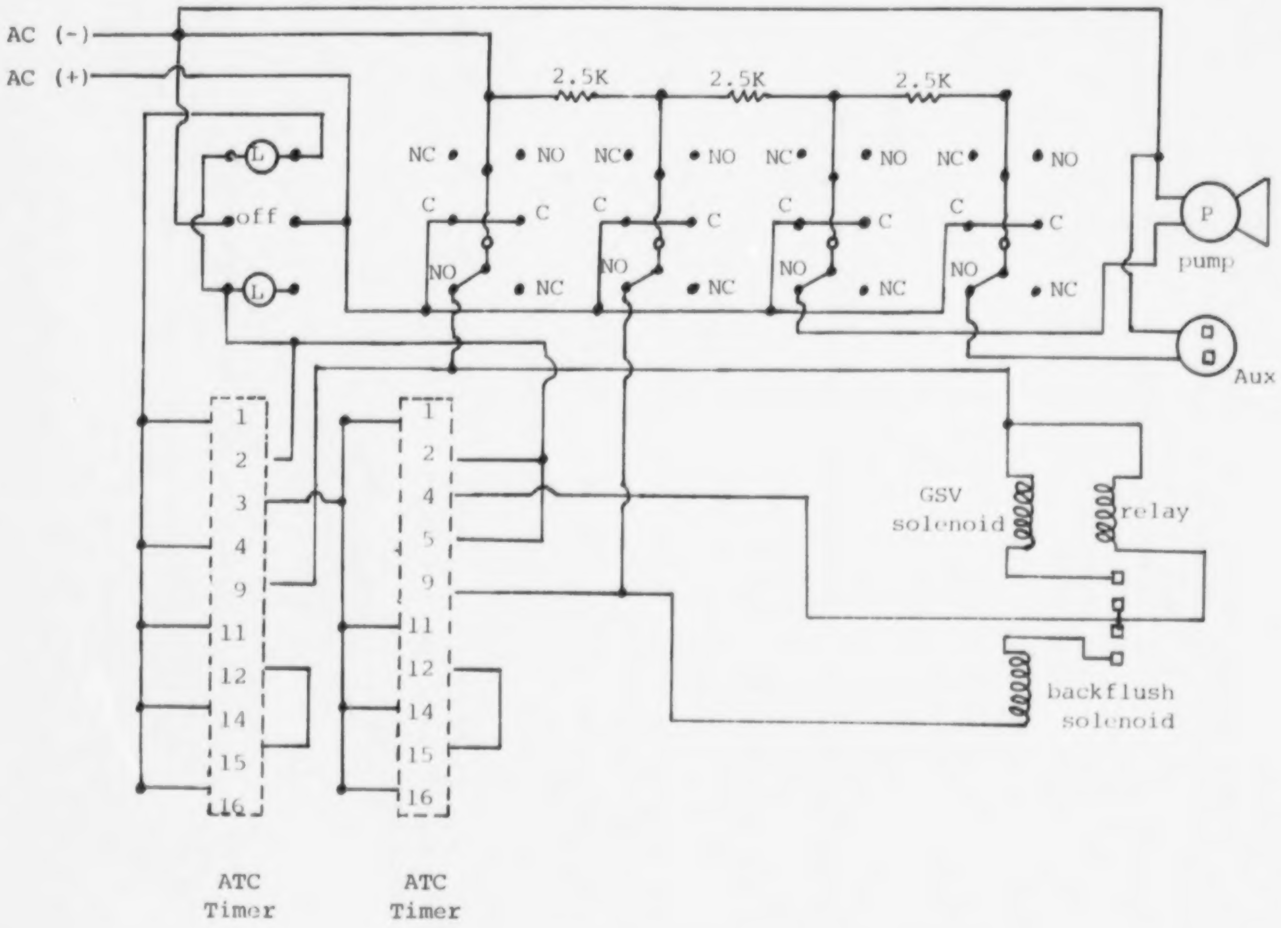

AC (-)
AC (+)
L
off
L
2.5K
2.5K
2.5K
NC
NO
C
NC
ATC Timer
ATC Timer
1
2
3
4
9
11
12
14
15
16
1
2
4
5
9
11
12
14
15
16
P
pump
Aux
GSV solenoid
relay
backflush solenoid

Figure 15. Electrical schematic for organic sulfide analysis system .

The next step is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92" Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sample in mℓ
V_{corr} = volume of gas sample in mℓ corrected to 68°F and 29.92" Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92" Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ \cancel{(ft^3)} \times 528°R}{T_{exp}\ (°R) \times 29.92\text{" Hg}}$$

[Equation 2]

Substituting Vol exp (mℓ) from Equation 1 into Equation 2 gives:

$$V_{corr}\ (mℓ) = \frac{P_{exp}\ (\text{"Hg}) \times F.R._{I}\ (mℓ/min) \times Ti\ (sec) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{" Hg} \times 60\ sec/min}$$

The next step converts the volume from mℓ to cubic meters by use of the conversion factor; 1 cubic meter = 10^6 mℓ.

$$V_{corr}\ (m^3) = \frac{P_{exp}\ (\text{"Hg}) \times F.R._{I}\ (mℓ/min) \times Ti\ (sec) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{" Hg} \times 60\ sec/min \times 10^6\ mℓ/m^3}$$

[Equation 3]

The next step is to find the μg of each of the sulfides in the Tenax trap. Since the FPD has a linear response in the region of concern, then the following equation holds:

$$\frac{\mu g_{sam}}{A_{sam}} = \frac{\mu g_{std}}{A_{std}}$$

μg_{sam} = μg sample in Tenax trap
A_{sam} = GC peak area of sample in relative units
μg_{std} = μg standard
A_{std} = GC peak area of standard in relative units

Solving for μg sample gives:

$$\mu g_{sam} = \frac{\mu g_{std} \times A_{sam}}{A_{std}}$$

(Equation 4)

The μg of standard for each of the organic sulfides is determined from the permeation rates of the permeation tubes containing each of the sulfides, the flow rate of the diluting gas, and the volume of gas sampled (10 mℓ).

$$\mu\text{g std} = \frac{\text{P.R. (ng/min)} \times 10\ \text{m}\ell}{\text{F.R.}_{\text{II}}\ (\text{m}\ell/\text{min}) \times 1000\ \text{ng}/\mu\text{g}}$$

[Equation 5]

P.R. (ng/min) = permeation rate of permeation tube at 40° in ng/min
10 mℓ = volume of calibration gas injected
F.R._{II} (mℓ/min)= flow rate of diluting gas for permeation system
1000 ng/μg = converts ng to μg, one μg equals 1000 ng

Substituting μg std from Equation 5 into Equation 4 gives:

$$\mu\text{g sam} = \frac{\text{P.R. (ng/min)} \times 10\ \text{m}\ell \times A_{\text{sam}}}{\text{F.R.}_{\text{II}}\ (\text{m}\ell/\text{min}) \times 1000\ \text{ng}/\mu\text{g} \times A_{\text{std}}}$$

[Equation 6]

To obtain μg sample/m^3, Equation 6 is divided by Equation 3 to give:

$$\mu\text{g sam}/\text{m}^3 = \frac{\text{P.R. (ng/min)} \times 10\ \text{m}\ell \times A_{\text{sam}} \times T_{\text{exp}}\ (^\circ\text{R})}{\text{F.R.}_{\text{II}}\ (\text{m}\ell/\text{min} \times 1000\ \text{ng}/\mu\text{g} \times A_{\text{std}} \times P_{\text{exp}}\ (\text{"Hg})}$$

$$\times \frac{29.92\text{" Hg} \times 60\ \text{sec/min} \times 10^6\ \text{m}\ell/\text{m}^3}{\text{F.R.}_{\text{I}}\ (\text{m}\ell/\text{min}) \times \text{Ti (sec)} \times 528^\circ\text{R}}$$

[Equation 7]

To find the concentration of each sulfide in ppm, the densities of the sulfides are needed. At 29.92" Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation

$$\frac{V}{T} = \frac{V_I}{T_I}$$

V_I = 22.4
T_I = 32°F + 460 = 492°R
V = volume at 68°F
T = 68°F + 460 = 528°R

Solving for V gives:

$$V = \frac{V_I \times T}{T_I} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04ℓ at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 24.04 ℓ/mole

$$\text{den } (\text{g}/\ell) = \frac{\text{mol. wt. g/mole}}{24.04\ \ \ell/\text{mole}}$$

The density in μg/mℓ can be found by converting g to μg and ℓ to mℓ as follows:

$$\text{den } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}} \times \frac{1 \times 10^{6} \mu g/g}{1 \times 10^{3} m\ell/\ell} = \frac{\text{mol. wt.} \times 1000}{24.04}$$

[Equation 8]

To obtain the concentration of each sulfide in ppm, the concentration in $\mu g/m^3$ is divided by the density in μg/mℓ

$$\text{ppm} = \mu g/m^{3} \div \mu g/m\ell = \frac{m\ell}{m^{3}}$$

Using Equations 7 and 8 gives the ppm concentrations in the form of the raw data.

$$\text{ppm} = \frac{\text{P.R. (ng/m}\ell) \times 10\ m\ell \times A_{sam} \times T_{exp}\ (°R) \times 29.92''\ Hg}{\text{F.R.}_{II}\ (m\ell/\text{min} \times 1000\ ng/\mu g \times A_{std} \times P_{exp}\ (''Hg)}$$
$$\times \frac{60\ \text{sec/min} \times 10^{6}\ m\ell/m^{3}}{\text{F.R.}_{I}\ (m\ell/\text{min}) \times Ti\ (\text{sec}) \times 528°R}$$
$$\times \frac{24.04\ \ell/\text{mole}}{\text{mol. wt. (g/mole)} \times 1000\ \mu g\text{-}\ell/g\text{-}m\ell}$$

[Equation 9]

At this point, the concentration can be expressed in $\mu g/m^3$ (Equation 7) and ppm (Equation 9) at 68°F and 29.92" Hg from the raw data.

Hewlett-Packard Calculations

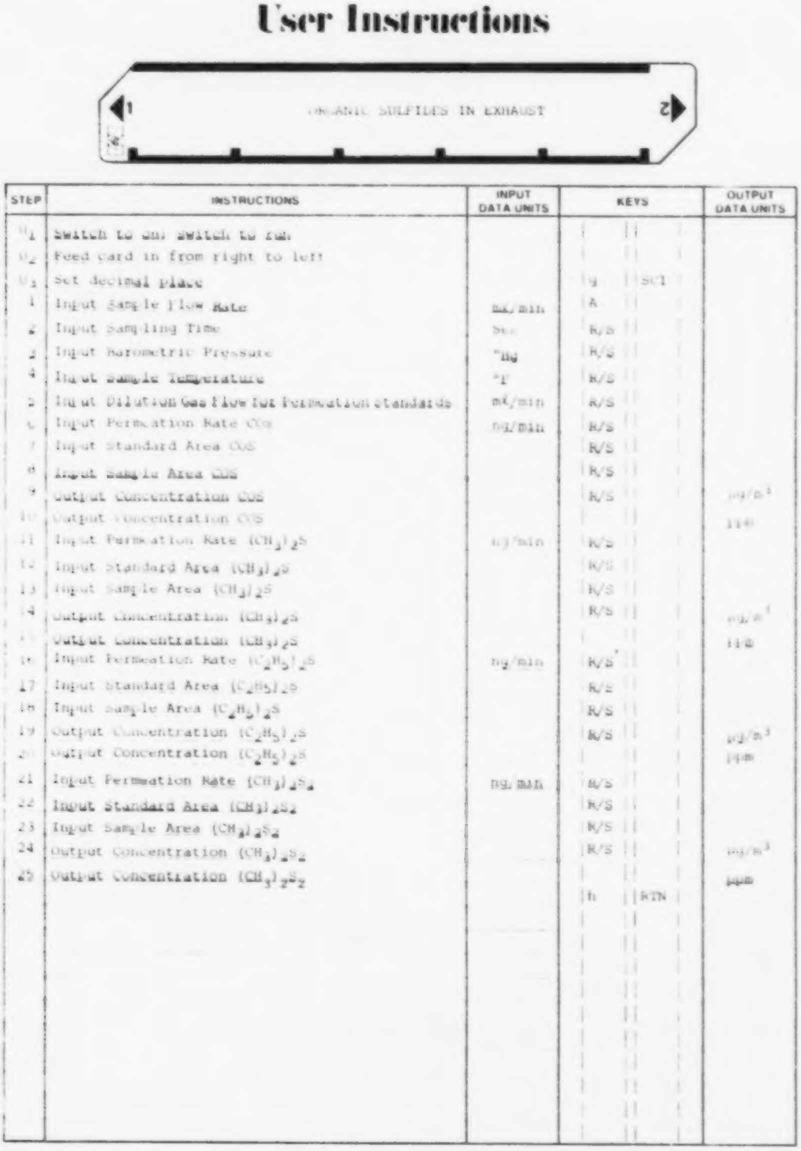
In order to insure maximum turnaround in a minimum time period, a Hewlett-Packard 67 program was developed to calculate the organic sulfide concentrations in $\mu g/m^3$ and ppm from the raw data. This program is presented in Figure 16.

Sample Calculation

Assume exhaust samples were collected in Tenax traps for each portion of a three-bag 1975 FTP. Raw data for these tests are presented in Figure 17. Calculations were performed using the HP-67 program and manual calculations.

Manual calculations for driving cycle FTP-1

$$\mu g/m^{3}\ \text{COS} = \frac{\text{P.R. (ng/m}\ell) \times 10\ m\ell \times A_{sam} \times T_{exp}\ (°R) \times 29.92''\ Hg}{\text{F.R.}_{II}\ (m\ell/\text{min}) \times 1000\ ng/\mu g \times \text{Astd} \times P_{exp}\ (''Hg)}$$
$$\times \frac{60\ \text{sec/min} \times 10^{6}\ m\ell/m^{3}}{\text{F.R.}_{I}\ (m\ell/\text{min}) \times Ti\ (\text{sec}) \times 528°R}$$
$$= \frac{667.5\ ng/m\ell \quad 10\ m\ell \times 30200 \times 535°R \times 29.92''\ Hg}{580\ m\ell/\text{min} \times 1000\ ng/\mu g \times 18514 \times 29.80''\ Hg}$$
$$\times \frac{60\ \text{sec/min} \times 10^{6}\ m\ell/m^{3}}{130\ m\ell/\text{min} \times 504 \times 528°R}$$



User Instructions

1 ORGANIC SULFIDES IN EXHAUST 2

STEP	INSTRUCTIONS	INPUT DATA UNITS	KEYS		OUTPUT DATA UNITS
0_1	Switch to on; switch to run				
0_2	Feed card in from right to left				
0_3	Set decimal place		g	SCI	
1	Input Sample Flow Rate	mℓ/min	A		
2	Input Sampling Time	sec	R/S		
3	Input Barometric Pressure	"Hg	R/S		
4	Input Sample Temperature	°F	R/S		
5	Input Dilution Gas Flow for Permeation standards	mℓ/min	R/S		
6	Input Permeation Rate COS	ng/min	R/S		
7	Input Standard Area COS		R/S		
8	Input Sample Area COS		R/S		
9	Output Concentration COS		R/S		µg/m³
10	Output Concentration COS				ppm
11	Input Permeation Rate $(CH_3)_2S$	ng/min	R/S		
12	Input Standard Area $(CH_3)_2S$		R/S		
13	Input Sample Area $(CH_3)_2S$		R/S		
14	Output Concentration $(CH_3)_2S$		R/S		µg/m³
15	Output Concentration $(CH_3)_2S$				ppm
16	Input Permeation Rate $(C_2H_5)_2S$	ng/min	R/S		
17	Input Standard Area $(C_2H_5)_2S$		R/S		
18	Input Sample Area $(C_2H_5)_2S$		R/S		
19	Output Concentration $(C_2H_5)_2S$		R/S		µg/m³
20	Output Concentration $(C_2H_5)_2S$				ppm
21	Input Permeation Rate $(CH_3)_2S_2$	ng/min	R/S		
22	Input Standard Area $(CH_3)_2S_2$		R/S		
23	Input Sample Area $(CH_3)_2S_2$		R/S		
24	Output Concentration $(CH_3)_2S_2$		R/S		µg/m³
25	Output Concentration $(CH_3)_2S_2$				ppm
			h	RTN	

Figure 16. HP-67 user instructions.

STEP	KEY ENTRY	KEY CODE	COMMENTS	STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	In Sample Flow, mℓ/min		×	71	
	3	03			R/S	84	Out µg/m³ $(C_2H_5)_2S$
	4	04			3	03	
	0	00		060	7	07	
	0	00			5	05	
	0	00			2	02	
	÷	81			÷	81	
	R/S	84	In Sampling Time, sec		R/S	84	Out ppm $(C_2H_5)_2S$ In PR $(CH_3)_2S_2$ ng/min
	×	71			RCL 2	34 02	
010	R/S	84	In Barometer, "Hg		×	71	
	×	71			R/S	84	In Std Area $(CH_3)_2S_2$
	STO 1	33 01			÷	81	
	R/S	84	In Sample Temp, °F		R/S	84	In Std Area $(CH_3)_2S_2$
	4	04		070	×	71	
	6	06			R/S	84	Out µg/m³ $(CH_3)_2S_2$
	0	00			3	03	
	+	61			9	09	
	RCL 1	34 01			1	01	
	h x⇄y	35 52			8	08	
020	÷	81			÷	81	
	h 1/x	35 62			R/S	84	Out ppm $(CH_3)_2S_2$
	R/S	84	In Dil Gas Flow, mℓ/min		h RTN	35 22	
	÷	81					
	STO 2	33 02		080			
	R/S	84	In Perm Rate COS, ng/min				
	RCL 2	34 02					
	×	71					
	R/S	84	In Std Area COS				
	÷	81					
030	R/S	84	In Sample Area COS				
	×	71					
	R/S	84	Out µg/m³ COS				
	2	02					
	4	04		090			
	9	09					
	9	09					
	÷	81					
	R/S	84	Out ppm COS In P.R. $(CH_3)_2S$, ng/min				
	RCL 2	34 02					
040	×	71					
	R/S	84	In Std Area $(CH_3)_2S$				
	÷	81					
	R/S	84	In Samp Area $(CH_3)_2S$				
	×	71		100			
	R/S	84	Out µg/m³ $(CH_3)_2S$				
	2	02					
	5	05					
	8	08					
	4	04					
050	÷	81	Out ppm $(CH_3)_2S$				
	R/S	84	In PR $(C_2H_5)_2S$, ng/min				
	RCL 02	34 02					
	×	71					
	R/S	84	In Std Area $(C_2H_5)_2S$	110			
	÷	81					
	R/S	84	In Samp Area $(C_2H_5)_2S$				

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9
A	B	C	D	E	I				

Figure 16 (cont'd). HP-67 program form

SWRI PROJECT NO.________ TEST NO.________ TEST DATE:________ VEHICLE:________

FUEL:______ CVS NO.______ TUNNEL SIZE:______ DRIVER:______ MILES:________

SAMPLE COLLECTION BY:______ CHEMICAL ANALYSIS BY:______ CALCULATIONS BY:________

GENERAL COMMENTS:________________________

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-2	FTP-3	SET-7	HFET	NYCC
Sample Flow Rate, mℓ/min	130	110	150	90	120	170
Sampling Time, sec	504	867	505	1397	765	1200
B.P., "Hg	29.80	30.03	29.02	29.25	29.95	29.50
Temp., °F	75	80	96	85	83	89
Dilution Gas Flow, mℓ/min	580	500	600	650	450	575
Permeation Rate COS, ng/min	667.5	667.5	667.5	667.5	667.5	667.5
Standard Area COS	19,514	20,112	21,238	16,542	15,962	23,146
Sample Area COS	30,200	40,100	33,162	20,122	16,269	32,641
Sample Conc. COS, $\mu g/m^3$	17.5	17.1	14.9	6.29	10.2	5.08
Sample Conc. COS, ppm	0.00700	0.00683	0.00598	0.00252	0.00406	0.00203
Permeation Rate $(CH_3)_2S$ ng/min	106[illegible]	1061	1061	1061	1061	1061
Standard Area $(CH_3)_2S$	41[illegible]	38,100	35,100	41,000	45,610	35,122
Sample Area $(CH_3)_2S$	[illegible]	40,381	49,162	38,142	54,753	41,611
Sample Conc. $(CH_3)_2S$, $\mu g/m^3$	[illegible]	14.4	21.3	7.65	19.0	6.78
Sample Conc. $(CH_3)_2S$, ppm	[illegible]	0.00556	0.00824	0.00296	0.00736	0.00262
Permeation Rate $(C_2H_5)_2S$, ng/min	445	445	445	445	445	445
Standard Area $(C_2H_5)_2S$	6971	7017	6844	6015	7113	7099
Sample Area $(C_2H_5)_2S$	31,649	34,650	32,111	7022	7914	17,416
Sample Conc. $(C_2H_5)_2S$, $\mu g/m^3$	32.5	28.2	29.9	4.03	7.39	5.89
Sample Conc. $(C_2H_5)_2S$, ppm	0.00865	0.00751	0.00798	0.00107	0.00197	0.00157
Permeation Rate $(CH_3)_2S_2$, ng/min	133.5	133.5	133.5	133.5	133.5	133.5
Standard Area $(CH_3)_2S_2$	2315	2210	2763	1651	1814	2917
Sample Area $(CH_3)_2S_2$	2011	3120	6372	1561	1418	2372
Sample Conc. $(CH_3)_2S_2$, $\mu g/m^3$	1.86	2.42	4.41	0.978	1.56	0.586
Sample Conc. $(CH_3)_2S_2$, ppm	0.000475	0.000617	0.00113	0.00250	0.000397	0.000149

Figure 17. Organic sulfide sample collection sheet.

$$= 17.5\ \mu g/m^3$$

$$\text{ppm COS} = \mu g/m^3 \div \text{density}\ \mu g/m\ell$$

$$\text{density}\ \mu g/m = \frac{\text{mol. wt. (COS)} \times 1000}{24.04\ell}$$

$$\text{mol. wt. COS} = 60.08\ g/mole$$

$$\text{density} = \frac{60.08\ g/mole \times 1000}{24.04\ \ell/mole} = 2499\ \mu g/m$$

$$\text{ppm} = 17.5\ \mu g/m^3 \div 2499\ \mu g/m\ell = 7.00 \times 10^{-3}\ m\ell/m^3 = 7.00 \times 10^{-3}\ \text{ppm}$$

The calculations for methyl sulfide, ethyl sulfide, and methyl disulfide are carried out in the same manner by substituting in the appropriate permeation rates, standard areas, sample areas, and molecular weights into the above formulas. These calculations give the following concentrations: $(CH_3)_2S$, 21.1 μg/m^3 and 0.00816 ppm; $(C_2H_5)_2S$, 32.5 μg/m^3 and 0.00865 ppm; and $(CH_3)_2S_2$, 1.86 μg/m^3 and 0.000475 ppm.

NOTE: The values used in these calculations are picked from a range of temperatures, pressures, etc. to validate the calculations and may not be representative of expected raw data. These calculations are presented to confirm that manual and HP-67 calculations give the same results. This was confirmed for six sets of calculations.

LIST OF EQUIPMENT

The analysis for the organic sulfides is performed using a gas chromatograph equipped with a flame photometric detector. The gas chromatograph, control console, sample collection, trap conditioning and trap preparation are the basic functions in the analysis. The major equipment required for each function is listed below.

Gas chromatograph and control console

1. Perkin-Elmer Model 3920B gas chromatograph equipped with a linearized flame photometric detector (FPD) and subambient temperature programmer.

2. Soltec dual channel recorder, Model B-281, 1 mv recorder.

3. Hewlett-Packard Model 3354 GC computer system with remote teletype printout.

4. Hewlett-Packard Model 1865A A/D converter.

5. Metronix Dynacalibrator Model 220-R for generation of organic sulfide standards.

6. Bendix valve oven.
7. Lindberg Furnace/Heavy Duty Model 55035.
8. Seiscor valve - gas sampling configuration
9. Seiscor valve - backflush configuration.
10. ATC timers, Model 325A346A10PX (2 ea.).
11. Analytical column, 6' x 1/8" Teflon, 60/80 Tenax-GC.
12. ASCO solenoid valve, Model 834501 (2 ea.).
13. Brooks flowmeter, R-2-15-A w/ss float, 0-150 scale.
14. Metal Bellows MB-158 pump.
15. Female quick-connect, stainless steel.
16. Nupro Model 2M stainless steel regulating valve.
17. Miscellaneous stainless steel, copper and Teflon tubing (1/8" and 1/6").
18. Miscellaneous stainless steel and brass unions, tees, etc.
19. Bud Classic II control console cabinet.
20. Miscellaneous electrical on-off switches.

Sampling

1. Perma Pure drier, Model PD 625 12S (17").
2. Brooks flowmeter, R-2-15-AAA, SS float, 0-150 scale.
3. Metal Bellows MB-158 pump.
4. Tenax-GC trap.
5. Sodium bicarbonate trap.
6. Miscellaneous stainless steel and Teflon tubing (1/16", 1/8" and 1/4").
7. Miniature stainless steel Swagelok female quick-connects.
8. Miniature stainless steel Swagelok male quick-connects.
9. Miscellaneous stainless steel and brass unions, tees, etc.

10. Stainless steel 7.0 cm flip-top filter.
11. Reeve Angel Type AH 7.0 cm fiber glass filters.
12. Nupro Model 4M stainless steel regulating valve.
13. Dewar flask, 1 quart capacity.

Trap Preparation and Conditioning System

1. Lindberg Furnace/Heavy Duty Model 55035.
2. Brooks flowmeter, R-2-15-A, glass float, 0-150 scale.
3. Nupro Model 4M brass regulating valve.
4. Swagelok 3/8" stainless steel reducing unions (2 per trap).
5. Stainless steel fritted discs, 50μ, 3/8" OD (2 per trap).
6. Stainless steel tubing, 2" x 3/8" OD (0.028" wall) (1 per trap).
7. Tenax-GC, 60/80 mesh (about 1 gram per trap).
8. Miscellaneous stainless steel and Teflon tubing (1/8" and 1/4").
9. Miscellaneous stainless steel and brass unions, tees, etc.
10. Asbestos gloves, pair.
11. Refillable plexiglass gas drier, 6".
12. Nupro in-line filter, brass, Model 4.

Expendables

1. Zero hydrogen gas (GC).
2. Zero air (GC).
3. Zero helium carrier gas (GC).
4. Nitrogen (Perma Pure drier).
5. Isopropyl alcohol, $CH_3CHOHCH_3$.
6. Sodium bicarbonate.
7. Dry ice.
8. Zero nitrogen (permeation system).

REFERENCES

Spencer, C. F., Baumann, F., and Johnson, J. F., Anal. Chem., Vol. 30, No. 9, pg. 1473, 1958.

Sumner, S., Karrman, K. J., and Sunden, V., Microchim Acta, pg. 1144, 1956.

Liberti, A. and Cartoni, G. P., Chim. e ind., Vol. 39, pg. 821, 1957.

Ryce, S. A. and Bryce, W. A., Anal. Chem., Vol. 29, pg. 925, 1957.

Desty, D. H. and Whyman, B. H. F., Anal. Chem., Vol. 29, pg. 230, 1957.

Coleman, H. J., Thompson, C. C. and Rall, H. T., Anal. Chem., Vol. 30, pg. 1592, 1958.

Desty, D. H. and Harbourn, C. L. A., Div. of Analytical and Petroleum Chemistry, Symposium on Advances in Gas Chromatography, 132nd meeting, ACS, N.Y, N. Y., September 1957.

Amberg, C. H., Can. J. Chem., Vol. 36, pg. 590, 1958.

Sullivan, J. H., Walsh, J. T., and Meritt Jr., C., Anal. Chem., Vol. 31, pg. 1827, 1959.

Dal Nogare, S. and Bennett, C. E., Anal. Chem., Vol. 30, pg. 1157, 1958.

Harrison, G. F., Knight, P., Kelly, R. P., and Heath, M. T., Second Int'l. Symposium on Gas Chromatography, Amsterdam, May 1958.

Adams, D. F. and Koppe, R. K., Tappi, Vol. 42, pg. 601, 1959.

Schols, J. A., Anal. Chem. Vol. 33, pg. 359, 1961.

Hall, H. L., Anal. Chem., Vol. 34, pg. 61, 1962.

Adams, D. F., Koppe, R. K., and Jungroth, D. M., Tappi, Vol. 43, pg. 602, 1960.

Feldstein, M., Balestrieri, S., and Levaggi, D. A., J. Air Poll. Cont. Assn., Vol. 15, pg. 215, 1965.

Fredericks, E. M. and Harlow, G. A., Anal. Chem. Vol. 36, pg. 263, 1964.

Mizany, A. I., J. Chromatog. Sci , Vol. 8, pg. 151, 1970

Kummer, W. A., Pitts Jr., J. N., and Steer, R. P., Environ. Sci. Tech., Vol.5, pg. 1045, 1971.

Rasmussen, R. A., Am. Lab, Vol. 4, pg. 55, 1972.

Brody, S. S. and Chaney, J. E., J. Gas Chromatog., Vol. 4, pg. 42, 1966.

Bruner, F., Liberti, A., Possanzini, M., and Allegrini, I., Anal. Chem., Vol. 44, pg. 2070, 1972.

Elliot, L. F. and Travis, T. A., Soil Sci. Soc. Amer. Proc., Vol. 37, pg. 700, 1973.

Francis, A. J., Adamson, J., Duxbury, J. M., and Alexander, M., Bull. Ecol. Res. Comm., (Stockholm), Vol. 17, pg. 485, 1973.

Lewis, J. A. and Papavizas, G. C., Soil Biol. Biochem., Vol. 2, pg. 239, 1970.

Lovelock, J. E., Maggs, R. J., and Rasmussen, R. A., Nature, London, Vol. 237, pg. 452, 1972.

Ronkainen, P., Denslow, J., and Leppanen, O., J. Chromatog. Sci., Vol. 11, pg. 384, 1973.

APPENDIX J

PHENOLS PROCEDURE

PHENOL PROCEDURE

Phenols (phenol; salicylaldehyde; m-cresol/p-cresol; p-ethylphenol/ 2-isopropylphenol/ 2,3-xylenol/3,5-xylenol/2,4,6-trimethylphenol; 2,3,5-trimethylphenol; and 2,3,5,6,-tetramethylphenol) in automotive exhaust can be sampled and quantitatively analyzed with a gas chromatograph (GC) equipped with a flame ionization detector. Dilute exhaust is passed through two Greenburg-Smith impingers in series, each containing 200 mℓ of 1 N KOH chilled in an ice bath. The contents of each impinger are acidified and extracted with ethyl ether. The samples are partially concentrated, combined and then further concentrated to about 1 mℓ. An internal standard is added and the volume is adjusted to 2 mℓ. The final sample is analyzed by the use of the GC and concentrations of individual phenols are determined by comparison to external and internal standards. The minimum detection limit is about 1 μg/mℓ.

SAMPLING SYSTEM

A schematic of the phenols sampling system is shown in Figure 1. As seen in the illustration, exhaust from the automobile is first diluted by the constant volume sample (CVS). The dilute exhaust entering the sampling probe is then filtered by a heated (375°F) Pallflex filter of porosity 1-100 μm to remove particulate from the gas stream. Next, a Thomas sample pump draws the exhaust through a heated sample line at about 0.8 ft^3/min. Both the filter and sampling line are heated to prevent phenol loss to condensation. The sample pump then pulls the warm exhaust through two impingers, each containing 200 mℓ of 1 N KOH chilled to ice bath temperatures (0-5°C). Wet exhaust exiting from the impingers passes through a molecular sieve/silica gel dryer before flowing through the sample pump, flowmeter and dry gas meter. The needle valve on the flowmeter controls flow through the sampling system and the dry gas meter measures the volume of gas in cubic feet that passes through the impingers. Gas temperature is measured by an iron-constantan thermocouple and can be monitored by a digital readout. Pictures of the phenol sampling cart are shown in Figure 2.

PROCEDURE

The flow schematic for the analysis of phenols is shown in Figure 3. This diagram describes sample treatment from collection to analysis. Diesel exhaust is first diluted in the constant volume sampler. Phenols present in the diluted exhaust are captured in two glass Greenburg-Smith impingers connected in series and chilled in an ice-water bath. Once collected, the samples are quantitatively transferred to 250 mℓ polyvinylchloride storage bottles.

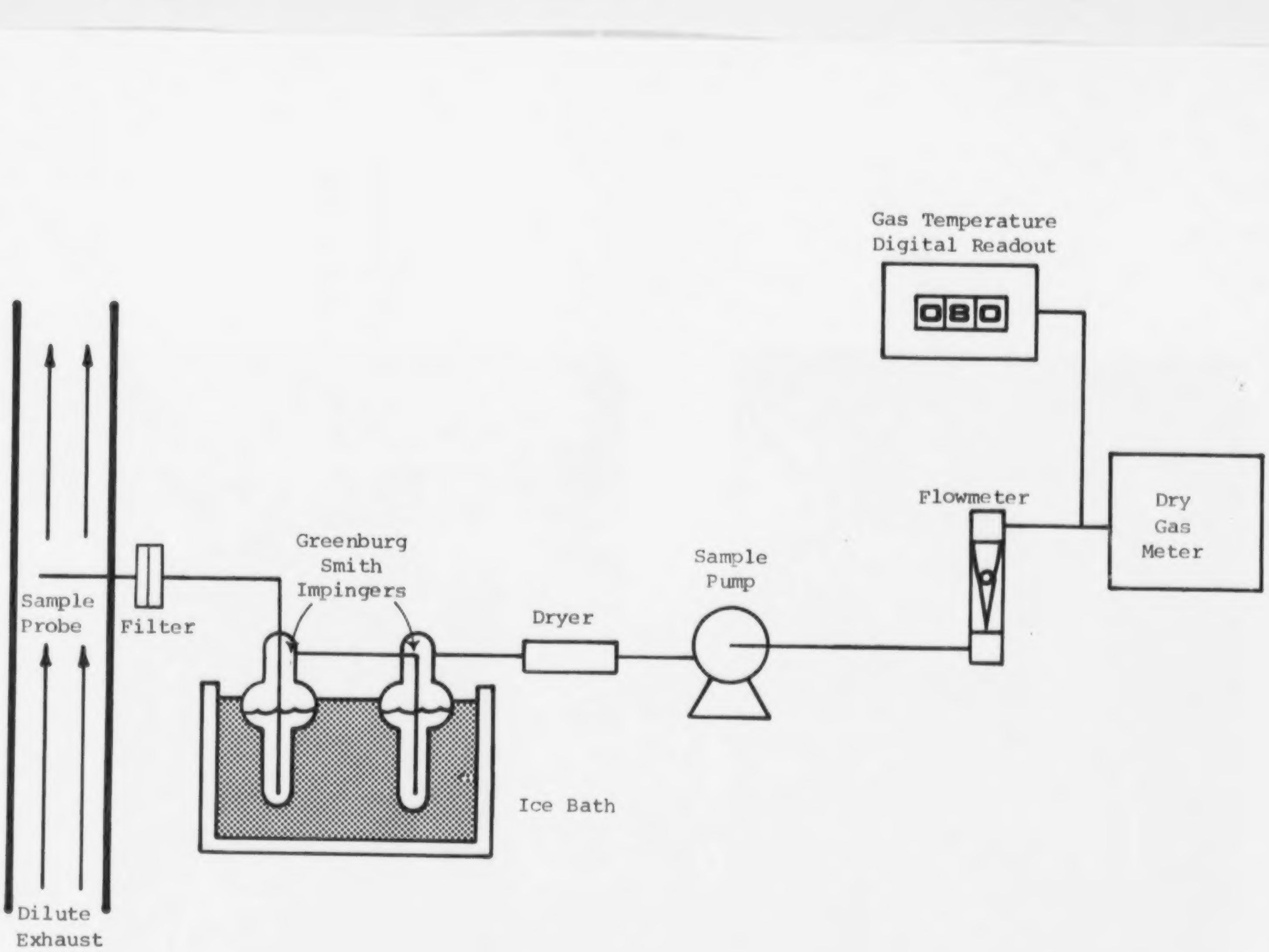

Gas Temperature
Digital Readout
080
Dry
Gas
Meter
Flowmeter
Sample
Pump
Dryer
Greenburg
Smith
Impingers
Ice Bath
Filter
Sample
Probe
Dilute
Exhaust

Figure 1. Phenols sample collection flow schematic.

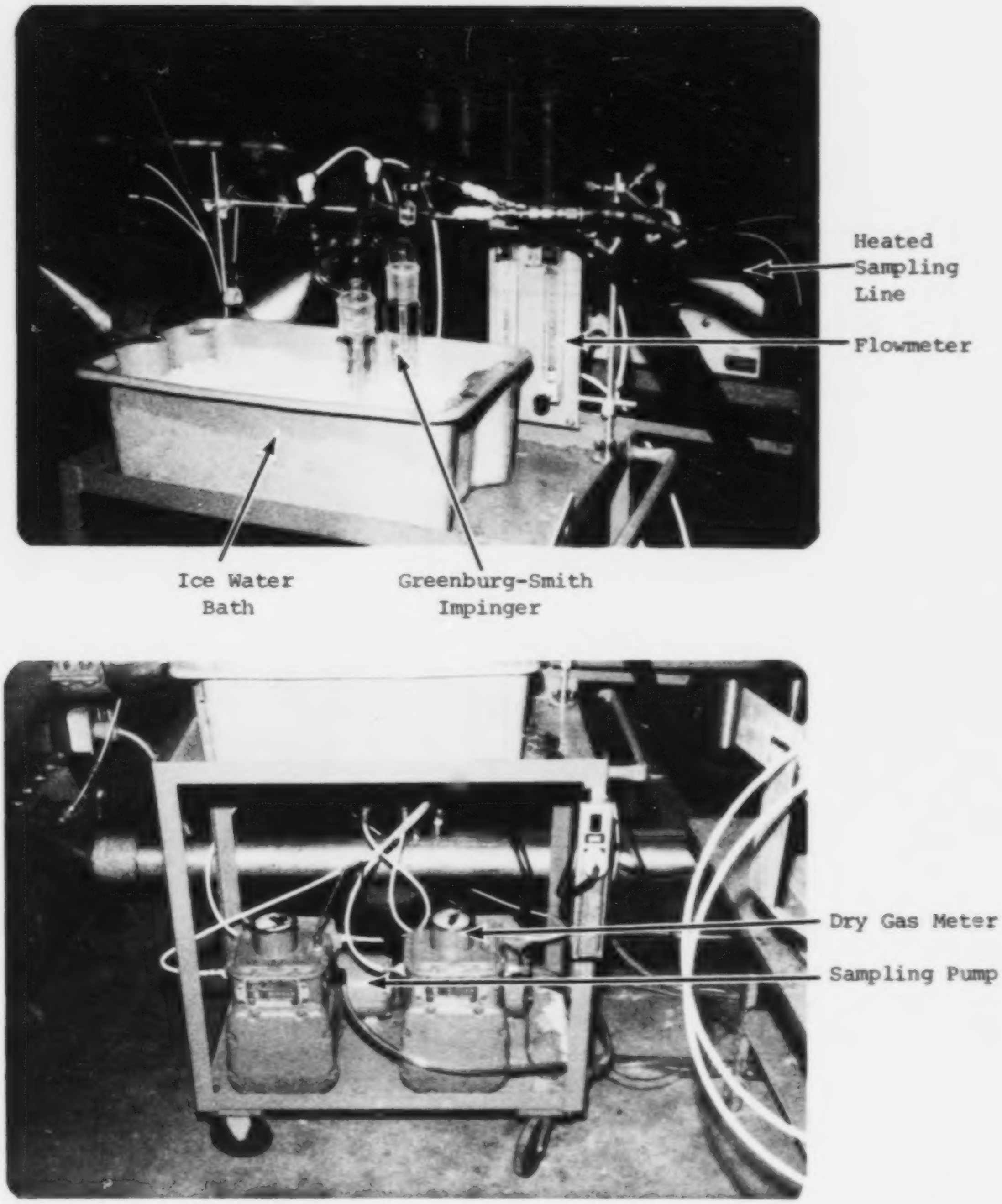

Heated
Sampling
Line
Flowmeter
Ice Water
Bath
Greenburg-Smith
Impinger
Dry Gas Meter
Sampling Pump

Figure 2. Phenols sampling system.

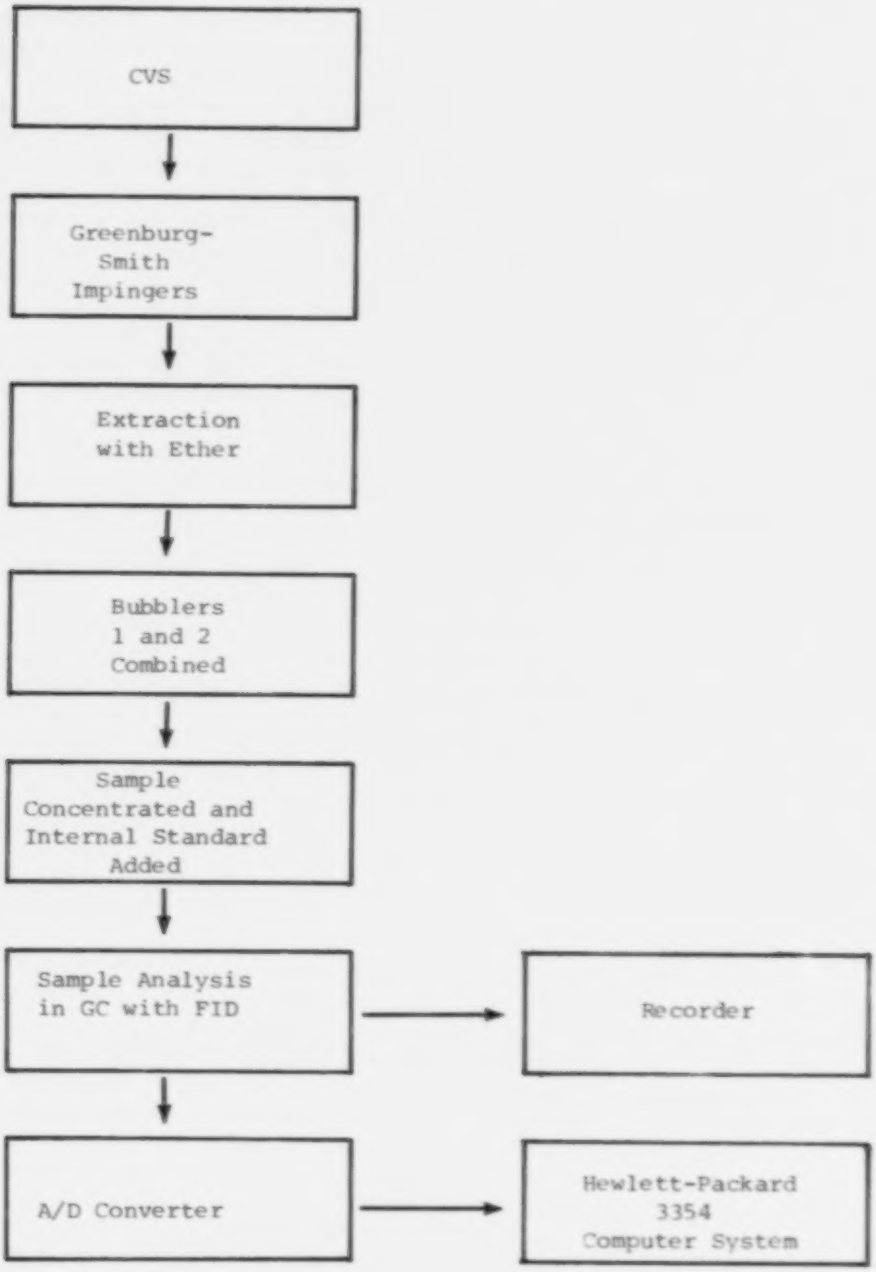

CVS
Greenburg-Smith Impingers
Extraction with Ether
Bubblers 1 and 2 Combined
Sample Concentrated and Internal Standard Added
Sample Analysis in GC with FID
Recorder
A/D Converter
Hewlett-Packard 3354 Computer System

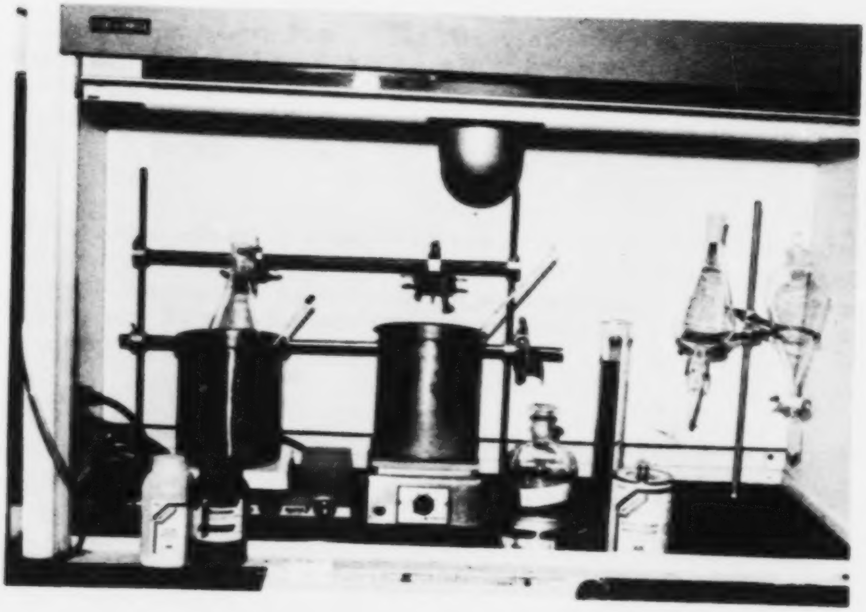
Figure 3. Phenols analysis flow schematic.

The entire workup procedure for phenols is carried out under a vented hood to prevent ether vapors from escaping into the room. Explosions can occur when handling ether, therefore,care needs to be taken not to heat samples to dryness. When ready for processing, the sample is poured into a 500 mℓ separatory funnel with 1 N KOH washings of the storage bottle. Thirteen milliliters of 50% H_2SO_4 is carefully pipeted into the funnel containing the sample and the flask is swirled and very gently shaken with venting until thoroughly mixed. Acidity is checked with litmus paper. Next, 200 mℓ of ethyl ether is added, again with swirling and gentle shaking and venting. When venting is no longer necessary the separatory funnel is shaken for two minutes and the two layers are allowed to separate. The bottom aqueous layer is drawn off into a second 500 mℓ separatory funnel and set aside. Anyhdrous Na_2SO_4 (9.4 g) is added to the phenolic ether mixture the first funnel with swirling and very gentle shaking and venting until venting is not needed. The contents are shaken for two minutes to remove traces of water. The dry ether and phenol mixture are transferred to a Kuderna Danish concentrator with washings. A boiling chip is added and the solvent volume is reduced to about one-fourth by heating in a 45°C water bath. The Kuderna concentrator is then set aside.

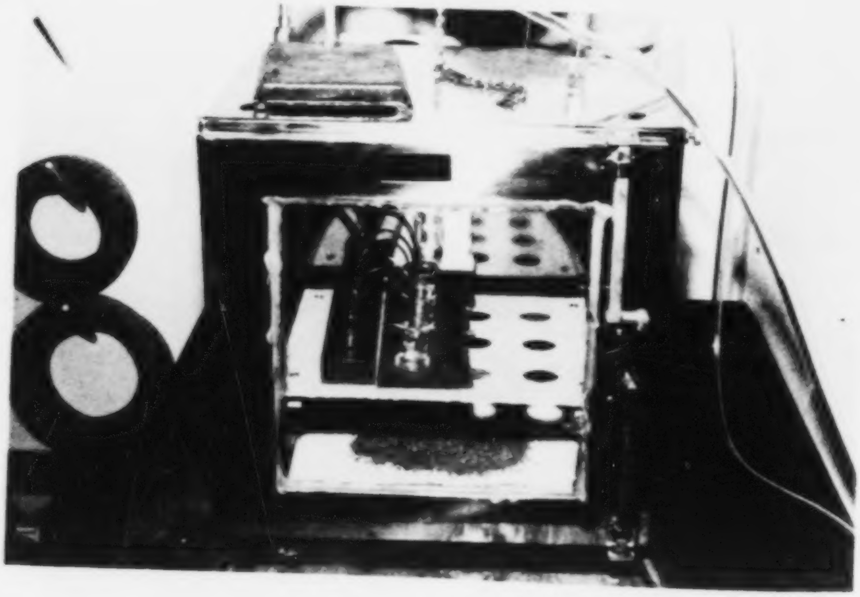
While the first ether portion is being heated, a second extraction is performed on the aqueous layer in the second separatory funnel. First, 100 mℓ of ether is added to the second funnel with swirling and gentle shaking and venting. When venting is unnecessary, the flask is shaken for two minutes. After the two layers have separated the bottom aqueous layer is drawn off and discarded. Anhydrous Na_2SO_4 (4.7 g) is added to the ether and phenols mixture and the funnel is swirled, gently shaken and vented. The flask is shaken for two minutes and the contents are then transferred with washings to the Kuderna concentrator containing the first ether extraction. A second boiling chip is added and the sample is concentrated to approximately 5 mℓ by means of the water bath. The concentrator is cooled to room temperature and the remaining sample is transferred to a 10 mℓ beaker for the final evaporation.

The last drying step is carried out is a desiccator box modified for nitrogen flow. A tray of molecular sieve and silica gel absorbs moisture that condenses on the beaker during the drying process. The nitrogen flow is directed into the 10 mℓ beakers containing the phenol sample by a six position manifold. The samples are placed under one of the curved needles on the manifold and the solvent is evaporated to about 1 mℓ by a stream of dry nitrogen. When the sample has warmed to room temperature (about 15 minutes) the concentrate is transferred to a 2 mℓ volumetric flask with small ether washings. The sample is then spiked with 100 µℓ of 300 µg/mℓ o-chlorophenol, the internal standard. The volume is adjusted to 2 mℓ with ether and the sample is labeled, sealed with Teflon tape and refrigerated until samples are ready for analysis. Several pictures of the equipment used in the workup of phenol exhaust samples are shown in Figure 4.

Phenol samples and standards are analyzed by a Perkin-Elmer 3920B gas chromatograph (GC) equipped with a flame ionization detector. The column used to separate phenols is a 6' x 1/8" Teflon column packed with 10% OS-138/H_3PO_4/SP-1200 on 100/120 mesh Chromosorb W AW. The carrier gas, zero nitrogen, flows through the column at 50 mℓ/min. The temperature of the



Extraction Apparatus



Sample Drying Chamber

Figure 4. Equipment used for workup of phenols samples.

column is programmed from 70-170°C at a rate of 4°C per minute with an initial hold at 70°C for 2 minutes. The purpose of temperature programming is to prevent the solvent peak from obscuring the phenol peaks and to allow better separation of phenols that elute at higher temperatures. The temperature of the injector and interface is maintained at 200°C. Samples and standards are usually analyzed at attention of X1 X8 or X1 X16 for 30 minutes. Injection volume is 1 μℓ. A picture of the analysis system is shown in Figure 5.

The external standard is injected first and response factors are determined from the concentrations and areas of each phenol. Then samples are injected and analyzed. Calculations are performed using sampling information and data obtained from the GC analyses. A chromatogram of the external standard is shown in Figure 6 and a chromatogram of a diesel exhaust sample is shown in Figure 7.

CALCULATIONS

The information obtained from the sampling system and the GC analysis of phenol samples is used to calculate the concentration of phenols in exhaust. The mathematical steps were programmed into a Hewlett-Packard 67 calculator for rapid data turnover. A copy of this program is shown in Figure 8. The concentration of individual phenols is determined by comparing the area of each phenol to the area of an internal standard, o-chlorophenol.

Different phenols do not give the same response to the flame ionization detector. Therefore, a correction needs to be incorporated into the calculation to account for this difference in response. This correction, termed the response factor, F, is determined by analyzing the external standard each day before sample analysis. The area per concentration unit of each individual phenol is compared to the per concentration unit of o-chlorophenol, the phenol used as the internal standard.

$$\text{Response factor (F)} = \frac{C_{px}}{A_{px}} \times \frac{A_{ocpx}}{C_{ocpx}}$$

where C_{px} = concentration of individual phenol in external standard, μg/mℓ
A_{px} = area produced by individual phenol in external standard, counts
A_{ocpx} = area produced by o-chlorophenol in external standard, counts
C_{ocpx} = concentration of o-chlorophenol in external standard, μg/mℓ

Response factors provide the means of calculating the concentration of the various phenols in the exhaust sample relative to only one phenol, the internal standard.

The concentration of any particular phenol in the exhaust sample in μg/mℓ is:

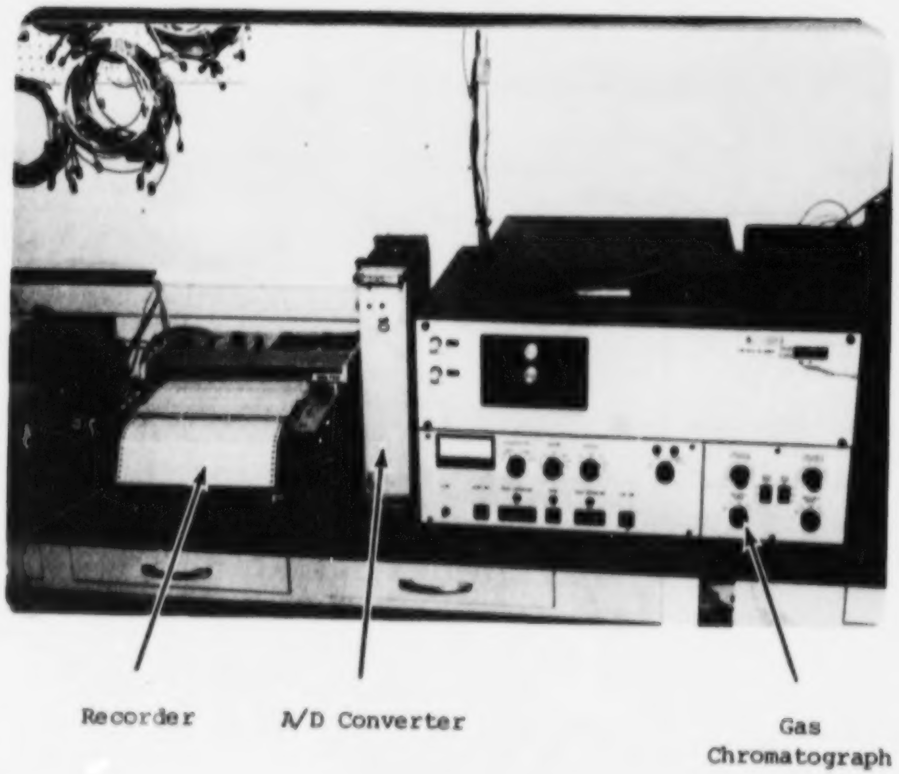
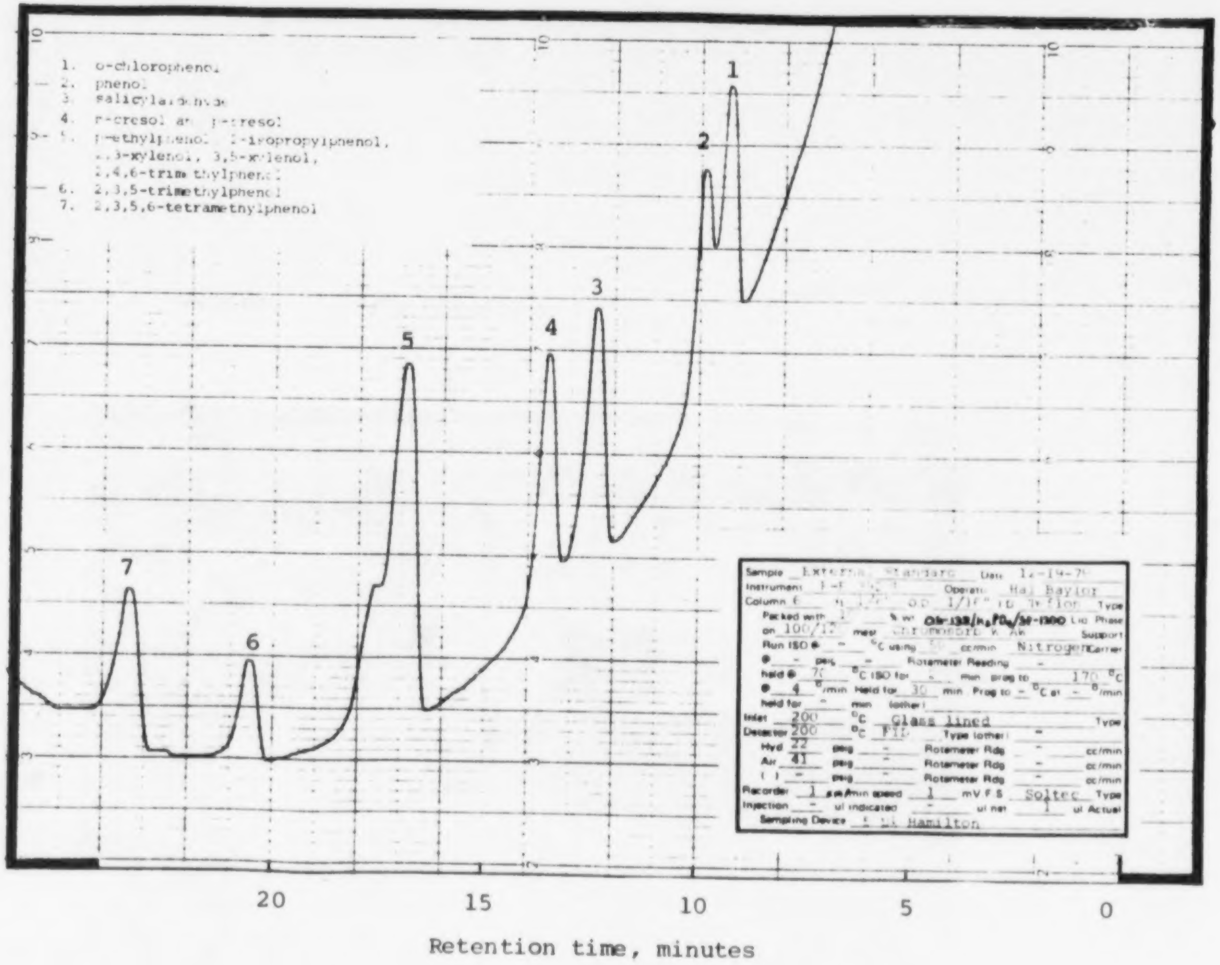

Recorder
A/D Converter
Gas
Chromatograph

Figure 5. Phenols analytical system.



Sample External Standard Date 12-19-7[illegible]
Instrument [illegible] Operator Hal Baylor
Column 6 ft 1/8" OD 1/16" ID Teflon Type
Packed with [illegible] % wt [illegible] Liq Phase
on 100/120 mesh Chromosorb W AW Support
Run ISO @ – °C using [illegible] cc/min Nitrogen Carrier
@ – psig – Rotameter Reading –
held @ 70 °C ISO for – min prog to 170 °C
@ 4 °/min Held for 30 min Prog to – °C at – °/min
held for – min (other)
Inlet 200 °C Glass lined Type
Detector 200 °C FID Type (other) –
Hyd 22 psig – Rotameter Rdg – cc/min
Air 41 psig – Rotameter Rdg – cc/min
( ) – psig – Rotameter Rdg – cc/min
Recorder 1 cm/min speed 1 mV F S Soltec Type
Injection – ul indicated – ul net 1 ul Actual
Sampling Device 1 ul Hamilton

Figure 6. Typical phenols external standard.

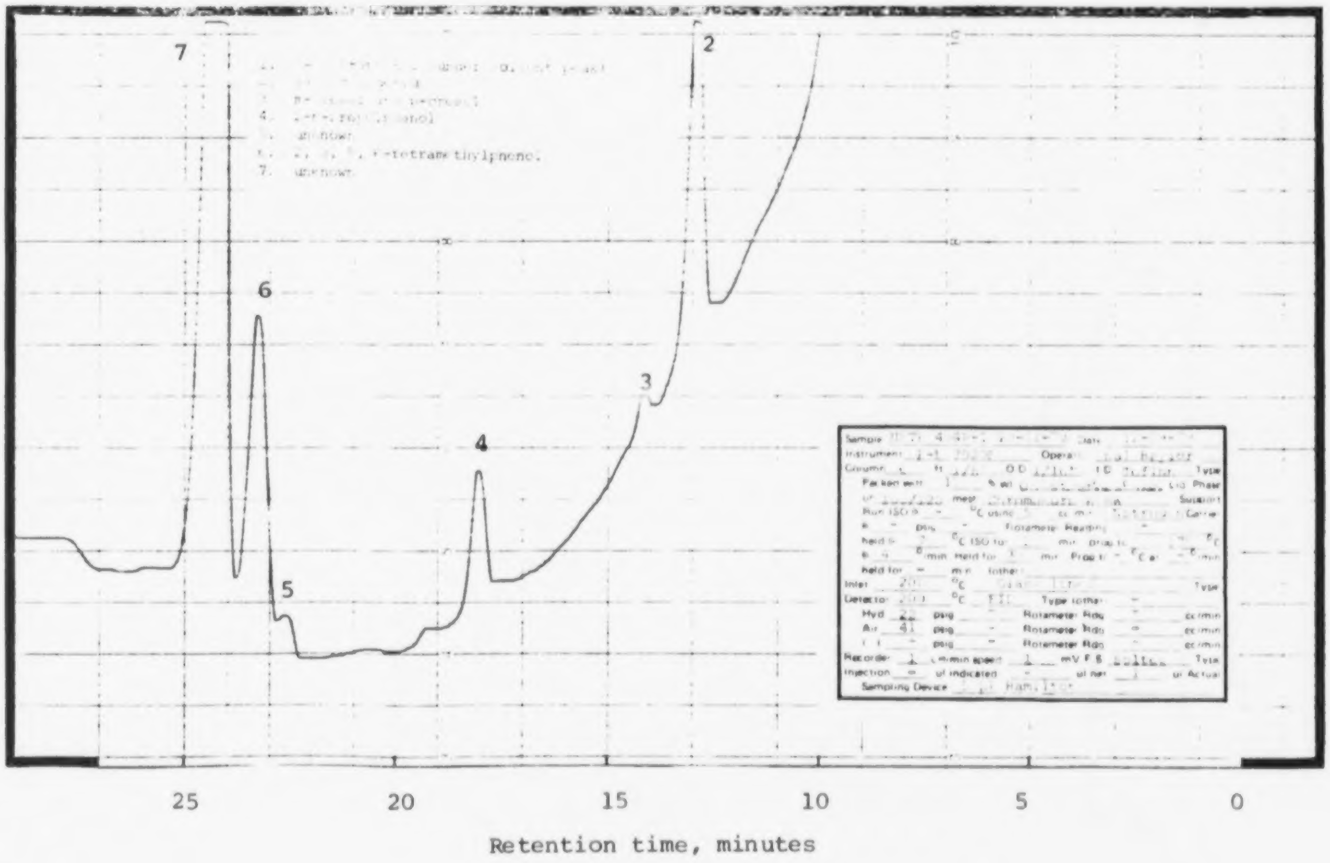
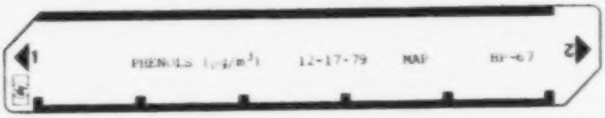


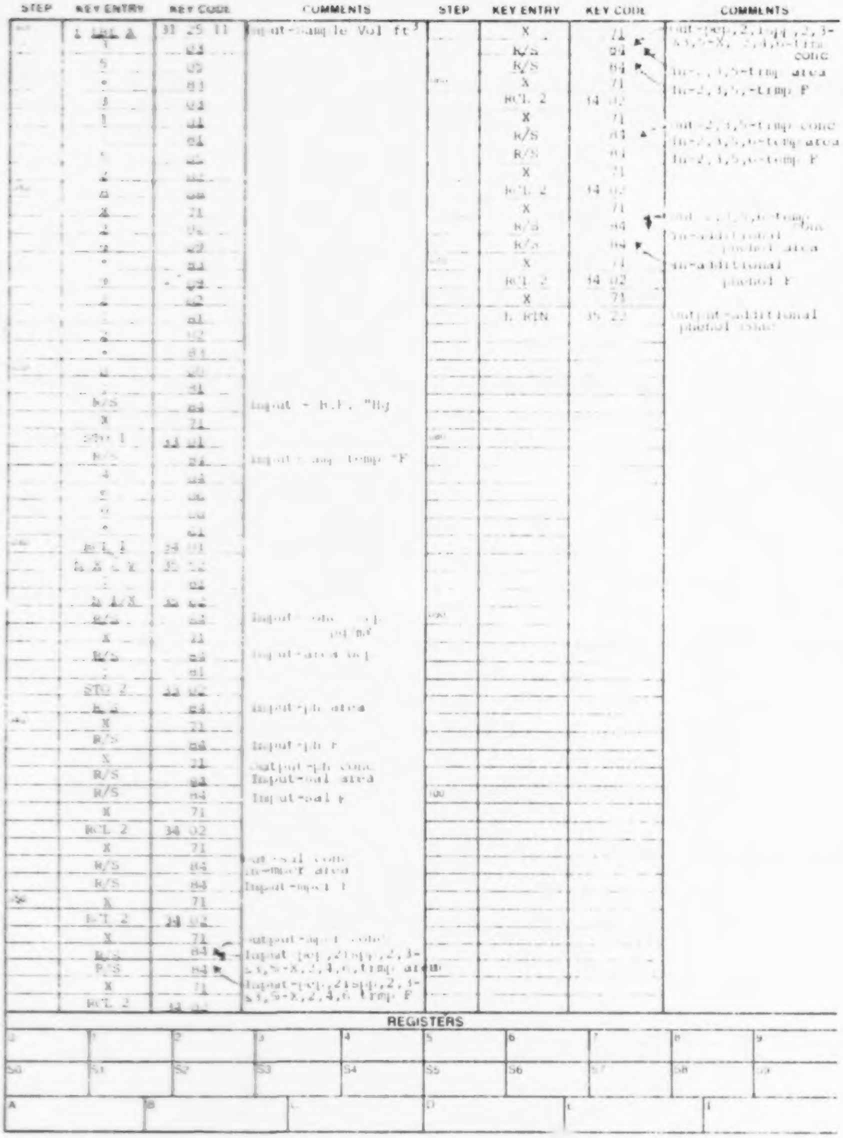
Figure 7. Typical diesel-CVS exhaust sample.

User Instructions



STEP	INSTRUCTIONS	INPUT DATA UNITS	KEYS	OUTPUT DATA UNITS
0_1	Switch to on, switch to run			
0_2	Feed card in from right to left			
0_3	set decimal place		DSP 0	
1	Input - Sample volume	ft^3	A	
2	Input - Barometric pressure	"Hg	R/S	
3	Input - Sample temperature	°F	R/S	
4	Input - Conc. of internal standard	µg/ml	R/S	
5	Input - Area of internal standard	counts	R/S	
6	Input - Phenol area	counts	R/S	
7	Input - F (phenol)		R/S	
8	Output - Phenol Conc.			$\mu g/m^3$
9	Input - Salicylaldehyde area	counts	R/S	
10	Input - F(salicylaldehyde)		R/S	
11	Output - Salicylaldehyde conc.			$\mu g/m^3$
12	Input - m-and p-cresols area	counts	R/S	
13	Input - F(m-and p-cresols)		R/S	
14	Output - m-and p-cresols conc.			$\mu g/m^3$
15	Input - p-ethylphenol, 2-isopropylphenol,		R/S	
	2,3-and 3,5-xylenols, 2,4,6-trimethylphenol area	counts		
16	Input - F(p-ethylphenol, 2-isopropylphenol,		R/S	
	2,3-and 3,5-xylehols, 2,4,6-trimethylphenol			
17	Output - p-ethylphenol, 2-isopropylphenol,		R/S	$\mu g/m^3$
	2,3-and 3,5-xylenols, 2,4,6,-trimethylphenol conc.			
18	Input - 2,3,5,-trimethylphenol area	counts	R/S	
19	Input - F(2,3,5,-trimethylphenol)		R/S	
20	Output - 2,3,5,-trimethylphenol conc.			$\mu g/m^3$
21	Input - 2,3,5,6,-tetramethylphenol area	counts	R/S	
22	Input - F(2,3,5,6,-tetramethylphenol)		R/S	
23	Output - 2,3,5,6,-tetramethylphenol conc.			$\mu g/m^3$
24	Input - additional phenol area	counts	R/S	
25	Input - F(additional phenol)		R/S	
26	Output - additional phenol conc.		h RTN	$\mu g/m^3$

Figure 8. HP-67 user instructions.



STEP	KEY ENTRY	KEY CODE	COMMENTS
	f LBL A	31 25 11	Input-sample Vol ft^3
	1	01	
	5	05	
	.	83	
	3	03	
	1	01	
	[illegible]	04	
	.	[illegible]	
	2	02	
	0	00	
	X	71	
	2	02	
	9	[illegible]	
	.	83	
	9	[illegible]	
	2	02	
	[illegible]	01	
	2	02	
	.	83	
	0	00	
	[illegible]	01	
	R/S	84	Input - B.P. "Hg
	X	71	
	STO 1	33 01	
	R/S	84	Input - samp. temp °F
	4	04	
	6	06	
	0	00	
	.	[illegible]	
	RCL 1	34 01	
	h X⇄Y	35 [illegible]	
	÷	81	
	h 1/X	35 [illegible]	
	R/S	84	Input- conc. [illegible] µg/m³
	X	71	
	R/S	84	Input-area [illegible]
	÷	81	
	STO 2	33 02	
	R/S	84	Input-ph area
	X	71	
	R/S	84	Input-ph F
	X	71	Output-ph conc
	R/S	84	Input-oal area
	R/S	84	Input-oal F
	X	71	
	RCL 2	34 02	
	X	71	out-oal conc
	R/S	84	in-m&p area
	R/S	84	Input-m&p F
	X	71	
	RCL 2	34 02	
	X	71	output-m&p conc
	R/S	84	Input [illegible],2,4[illegible],2,3-[illegible],5-X,2,4,6,trmp area
	R/S	84	Input-[illegible],2,4[illegible],2,3-[illegible],5-X,2,4,6 trmp F
	X	71	
	RCL 2	34 02	
	X	71	out-[illegible],2,4[illegible],2,3-[illegible],5-X, 2,4,6-trm conc
	R/S	84	
	R/S	84	in-2,3,5-trmp area
	X	71	in-2,3,5,-trmp F
	RCL 2	34 02	
	X	71	out-2,3,5-trmp conc
	R/S	84	in-2,3,5,6-tetrp area
	R/S	84	in-2,3,5,6-temp F
	X	71	
	RCL 2	34 02	
	X	71	out-2,3,5,6-temp conc
	R/S	84	in-additional phenol area
	R/S	84	
	X	71	in-additional phenol F
	RCL 2	34 02	
	X	71	
	h RTN	35 22	output-additional phenol conc

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9
A	B	C	D	E	I				

Figure 8 (Cont'd). HP-67 program form.

$$\frac{C_{ocps}}{A_{ocps}} \times A_{sa} \times F$$

where A_{sa} = area produced by the phenol in the sample, counts
A_{ocps} = area produced by o-chlorophenol in the sample, counts
C_{ocps} = concentration of o-chlorophenol in the sample, μg/mℓ

The extraction process involves concentrating the phenols from 200 mℓ in the impingers to 2 mℓ in the final sample. The weight in μg of the phenol in the impingers is given by

$$\frac{C_{ocps}}{A_{ocps}} \times A_{sa} \times F \times V_{sa}$$

where V_{sa} = final sample volume, mℓ.

Equation 1

To determine the concentration of phenols in dilute exhaust the volume of exhaust passing through the impingers has to be measured. This volume, measured at ambient conditions, is corrected to standard conditions (68°F and 29.92" Hg).

$$\frac{P_{am} \times V_{am}}{T_{am} + 460} = \frac{P_{stp} \times V_{stp}}{T_{stp}}$$

where P_{am} = barometric pressure at ambient, "Hg
V_{am} = volume at ambient, ft^3
T_{am} = temperature at ambient, °F
P_{stp} = standard barometric pressure, 29.92 "Hg
V_{stp} = volume at 68°F and 29.92 "Hg
T_{stp} = standard temperature, 68°F + 460 = 528°R.

Rearranging and converting ft^3 to m^3,

$$V_{stp} = \frac{P_{am}}{P_{stp}} \times \frac{T_{stp}}{(T_{am} + 460)} \times \frac{V_{am}}{35.31\ ft^3/m^3}.$$

Equation 2

Dividing the weight of the phenol captured in the impingers in Equation 1 by the volume of dilute exhaust passed through the bubblers in Equation 2 yields the concentration of the phenol in dilute exhaust in $\mu g/m^3$.

$$\frac{\frac{C_{ocps}}{A_{ocps}} \times A_{sa} \times F \times V_{sa}}{\frac{P_{am}}{P_{stp}} \times \frac{T_{stp}}{(T_{am} + 460)} \times \frac{V_{am}}{35.31\ ft^3/m^3}}$$

$$= \frac{C_{ocps,}\ \mu g/m\ell \times A_{sa,}\ \text{counts} \times F \times V_{sa,}\ m\ell}{A_{ocps,}\ \text{counts}}$$

$$\times \frac{29.92\ \text{"Hg} \times (T_{am,}\ {}^{\circ}F + 460) \times 35.31\ ft^3/m^3}{P_{am,}\ \text{"Hg} \times 528{}^{\circ}R \times V_{am,}\ ft^3}$$

Equation 3

Equation 3 yields the concentration of phenols that the Hewlett-Packard 3354 computer identifies as separate peaks. However, two peaks found in several exhaust samples may contain more than one phenol, in which case an average response factor is used to calculate the concentration. For example, m-cresol and p-cresol elute at the same time. The response factor is determined by comparing the area of the cresols peak per total concentration unit of the two cresols to the area per concentration unit of o-chlorophenol. This method is the same used for only one phenol except that the concentrations of all the phenols under the peak are added together. In the case of multiple phenols under a single peak, the calculated concentration represents the total concentration of all the phenols eluting at that retention time. One additional peak represents more than one phenol. The phenols eluting under the same peak are p-ethylphenol, 2-isopropylphenol, 2,3-dimethylphenol, 3,5-dimethylphenol and 2,4,6-trimethylphenol. All of these compounds are not necessarily found in automotive exhaust, but since separation of them is not possible using the specified equipment and instrument conditions, it can only be assumed that they are all present. Individual phenols that have been recovered from exhaust are phenol, salicylaldehyde, 2,3,5,-trimethylphenol and 2,3,5,6,-tetramethylphenol.

Sample Calculation

Two sample calculations will be performed using the raw data from the data sheet shown in Figure 9. The information contained in the data sheet is not necessarily data obtained during an actual test. The values were presented mainly as an aid to demonstrate the calculation of phenols concentrations from raw data. Experimental values are plugged into Equation 3 and the calculations are performed to give answers in $\mu g/m^3$.

Example 1

During an FTPh driving cycle, assume that 17.483 ft^3 of dilute exhaust is passed through two impingers containing 200 mℓ of 1 N KOH. Ambient temperature and pressure were reported to be 79°F and 29.27 "Hg, respectively. Before final concentration 100 µℓ of the 200 µg/mℓ internal standard was added and the volume was adjusted to 2 mℓ. The internal standard, at a concentration of 10 µg/mℓ in the final sample, produced an area response of 2159 counts. The response factor and area of each phenol are listed on the following page.

SWRI PROJECT NO. ________ TEST NO. ________ TEST DATE: ________ VEHICLE: ________

FUEL: ______ CVS NO. ______ TUNNEL SIZE: ______ DRIVER: ________ MILES: ________

SAMPLE COLLECTION BY: ________ CHEMICAL ANALYSIS BY: ______ CALCULATIONS BY: ______

GENERAL COMMENTS: ____

Test No.	1	2	3	4	5	6
Driving Cycle	FTPc	FTPh	SET 7	FET	NYCC	85 kph
Volume, ft^3	17.582	17.483	18.400	10.435	8.126	18.567
B.P., "Hg	29.27	29.27	29.27	29.27	29.27	29.27
Temp. °F	77	79	79	78	80	80
Final Sample Vol. (mℓ)	2	2	2	2	2	2
Conc. Internal Std. (μg/mℓ)	10	10	10	10	10	10
Area Internal Std.	2400	2159	2262	2109	2387	2182
Area Phenol	1373	2209	1070	879	500	758
F Phenol	0.8354	0.8354	0.8379	0.8348	0.8299	0.8350
$\mu g/m^3$ Phenol	20	36	16	25	16	12
Area Salicylaldehyde	1457	6401	2078	6006	2868	3543
F Salicylaldehyde	0.5079	0.5140	0.4980	0.5136	0.5200	0.5092
$\mu g/m^3$ Salicylaldehyde	13	64	18	103	57	33
Area m-and p-cresols	1023	1227	986	1500	3274	2921
F m- and p-cresols	0.4232	0.5105	0.4657	0.5033	0.4451	0.4079
$\mu g/m^3$ m- and p-cresols	8	12	8	25	55	22
Area pep, 2ispp, 2,3 -& 3,5 -X, 2,4,6-trmp	412	2029	1569	1283	2433	4155
F pep, 2ispp, 2,3-& 3,5-X, 2,4,6-trmp	0.7778	0.7864	0.7680	0.8107	0.7776	0.8091
$\mu g/m^3$ pep, 2ispp, 2,3-&3,5 -X, 2,4,6,-trmp	6	31	21	35	72	61
Area 2,3,5-trmp	876	1443	2785	2235	2567	2488
F 2,3,5-trmp	0.5010	0.4766	0.5284	0.4546	0.5160	0.5518
$\mu g/m^3$ 2,3,5-trmp	8	13	26	34	50	25
Area 2,3,5,6,-temp	1167	2382	1771	4067	3852	981
F 2,3,5,6,-temp	0.6342	0.6140	0.5865	0.6676	0.5744	0.6020
$\mu g/m^3$ 2,3,5,6,-temp	13	29	18	91	84	11
Area additional phenol	-	-	-	-	-	-
F Additional phenol	-	-	-	-	-	-
$\mu g/m^3$ additional phenol	-	-	-	-	-	-

Figure 9. Phenol data sheet.

Phenol	F	Area
Phenol	0.8345	2209
Salicylaldehyde	0.5140	6401
m-cresol and p-cresol	0.5105	1227
p-ethylphenol, 2-isopropylphenol, 2,3- and 3,5-xylenol, 2,4,6-trimethylphenol	0.7864	2029
2,3,5-trimethylphenol	0.4766	1443
2,3,5,6-tetramethylphenol	0.6140	2382

The appropriate values are plugged into Equation 3 for each phenol.

Phenol

$$\frac{10\ \mu g/m\ell \times 2209\ \text{counts} \times 0.8345 \times 2.0\ m\ell}{2159\ \text{counts}}$$

$$\times \frac{29.92\ \text{"Hg} \times (79°\text{F} + 460) \times 35.31\ \text{ft}^3/\text{m}^3}{29.27\ \text{"Hg} \times 528°\text{R} \times 17.483\ \text{ft}^3}$$

$= 36\ \mu g/m^3$ phenol

Salicylaldehyde

$$\frac{10\ \mu g/m\ell \times 6401\ \text{counts} \times 0.5140 \times 2.0\ m\ell}{2159\ \text{counts}}$$

$$\times \frac{29.92\ \text{"Hg} \times (79°\text{F} + 460) \times 35.31\ \text{ft}^3/\text{m}^3}{29.27\ \text{"Hg} \times 528°\text{R} \times 17.483\ \text{ft}^3}$$

$= 64\ \mu g/m^3$ salicylaldehyde

m-cresol and p-cresol = $12\ \mu g/m^3$

p-ethylphenol, 2-isopropylphenol, 2,3- and 3,5-xylenol and 2,4,6-trimethylphenol

$$\frac{10\ \mu g/m\ell \times 2029\ \text{counts} \times 0.7864 \times 2.0\ m\ell}{2159\ \text{counts}}$$

$$\times \frac{29.92\ \text{"Hg} \times (79°\text{F} + 460) \times 35.31\ \text{ft}^3/\text{m}^3}{29.27\ \text{"Hg} \times 528°\text{R} \times 17.483\ \text{ft}^3}$$

$= 31\ \mu g/m^3$ p-ethylphenol, 2-isopropylphenol, 2,3- and 3,5-xylenol,
2,4,6-trimethylphenol

2,3,5-trimethylphenol = $13\ \mu g/m^3$

2,3,5,6-tetramethylphenol = $29\ \mu g/m^3$

Example 2

Suppose that during the FTPc driving cycle 17.582 ft^3 of dilute exhaust measured at 29.27 "Hg and 77°F passed through two impingers. The sample was processed and analyzed following the phenols procedure. The 10 μg/mℓ internal standard gave a responce of 2400 counts. The response factors and areas of the other phenols are listed below.

Phenol	F	Area
Phenol	0.8354	1373
Salicyaldehyde	0.5079	1457
m-cresol and p-cresol	0.4232	1023
p-ethylphenol, 2-isopropylphenol, 2,3-and 3,5-xylenol and 2,4,6-trimethylphenol	0.7778	412
2,3,5-trimethylphenol	0.5010	876
2,3,5,6-tetramethylphenol	0.6342	1167

Phenol

$$\frac{10\ \mu g/m\ell \times 1373\ \text{counts} \times 0.8354 \times 2.0\ m\ell}{2400\ \text{counts}}$$

$$\times\ \frac{29.92\ \text{"Hg} \times (77°F + 460) \times 35.31\ ft^3/m^3}{29.27\ \text{"Hg} \times 528°R \times 17.582\ ft^3}$$

$$=\ 20\ \mu g/m^3\ \text{phenol}$$

Salicylaldehyde

$$\frac{10\ \mu g/m\ell \times 1457\ \text{counts} \times 0.5079 \times 2.0\ m\ell}{2400\ \text{counts}}$$

$$\times\ \frac{29.92\ \text{"Hg} \times (77°F + 460) \times 35.31\ ft^3/m^3}{29.27\ \text{"Hg} \times 528°R \times 17.582\ ft^3}$$

$$=\ 13\ \mu g/m^3\ \text{salicylaldehyde}$$

m-cresol and p-cresol

$$\frac{10\ \mu g/m\ell \times 1023\ \text{counts} \times 0.4232 \times 2.0\ m\ell}{2400\ \text{counts}}$$

$$\times\ \frac{29.92\ \text{"Hg} \times (77°F + 460) \times 35.31\ ft^3/m^3}{29.27\ \text{"Hg} \times 528°R \times 17.582\ ft^3}$$

$$=\ 8\ \mu g/m^3\ \text{m-cresol and p-cresol}$$

p-ethylphenol, 2-isopropylphenol, 2,3-and 3,5-xylenol and 2,4,6,-trimethylphenol

$$\frac{10\ \mu g/m\ell \times 412\ \text{counts} \times 0.7778 \times 2.0\ m\ell}{2400\ \text{counts}}$$

$$\times\ \frac{29.92\ \text{"Hg} \times (77°F + 460) \times 35.31\ ft^3/m^3}{29.27\ \text{"Hg} \times 528°R \times 17.572\ ft^3}$$

$= 6\ \mu g/m^3$ p-ethylphenol, 2-isopropylphenol, 2,3-and 3,5-xylenol, 2,4,6,-trimethylphenol

2,3,5-trimethylphenol = 8 $\mu g/m^3$

2,3,5,6-tetramethylphenol = 13 $\mu g/m^3$

LIST OF EQUIPMENT

The equipment needed for collection, workup and analysis of phenols in exhaust is listed below in separate sections. The manufacturer, catalog or model number and description are given for each entry.

Sampling

1. Greenburg-Smith glass impingers, Houston Glass Fabricating, Catalog #310610-0028, arm joints 28/15, bottle joint 45/50.

2. Ground glass socket joint with arm modified to 5/16", Houston Glass Fabricating, Catalog #285045, 28/12 socket.

3. Ground glass ball joint with arm modified to 5/16", Houston Glass Fabricating, Catalog # 285040, 28/12 ball.

4. L-shaped glass connecting adapter, Houston Glass Fabricating, Catalog #015639, male and female size 28/12.

5. U-shaped glass connecting adpater, Houston Glass Fabricating, Catalog #160719 size 28/15 male-male socket joint, 2.25" center to center length.

6. Thomas ball and socket joint clamp, Houston Glass Fabricating, Catalog # 285100 size 28.

7. Class A, 2000 mℓ volumetric flask.

8. Flowmeters, Brooks Instrument Division, Kynar, Sho-Rate "150" with R-6-15-B metering tube, stainless steel ball, 1-92 CFH range, graduated 1-100.

9. Dry gas meter, American Singer Corporation, Type Al-120, 60 CFH capacity.

10. Sample pump, Thomas Model #727CA39, 1 ft^3/min free flow capacity.

11. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long.

12. Teflon tubing, United States Plastic Corporation, 5/16" OD x 1/8" ID and 3/8" OD x 1/4" ID.

13. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps and connectors, etc.

14. Miscellaneous electrical switches, lights, wiring, etc.

15. Miscellaneous Swagelok fittings.

16. Athena temperature controller, Technical Heaters Incorporated, Model 6000, 100-600°F range, 110 volts.

17. Heated sample line, Technical Heaters Incorporated, Catalog #LP-212-8-5, 5' length, 13/32" hose with 1/2" tube end stainless steel fittings.

18. Pallflex Fiberfilm filters, Pallflex Products Corporation, Catalog #T60A20, 70 mm diameter.

19. 250 mℓ polyvinylchloride sample storage bottles, Nalgene Labware, Catalog #2000-0008.

20. Iron/constantan type J single thermocouple, Thermo Sensors Corp.

Workup

1. Pear shaped 500 mℓ separatory funnel, Houston Glass Fabricating, Catalog #260145, with Teflon stopcock.

2. Class A, 3 and 10 mℓ volumetric pipets.

3. Safety bulb for pipetting, Markson Science Supplies, Catalog #E-8074.

4. Miscellaneous glass beakers.

5. 250 mℓ glass graduated cylinder.

6. Basic indicating litmus paper.

7. Ring stands.

8. Kuderna Danish Concentrator, Ace Glass Incorporated, Catalog #6708-03 and 6708-35.

9. Boileezers boiling chips, Fisher Scientific Company, Catalog #B-365.

10. Hot plate with heat control.

11. 2000 mℓ beaker for water bath.

12. 10 mℓ glass beakers with pouring spout.

13. Disposable transfer pipets, Curtin Matheson Scientific Incorporated, Catalog #269-175.

14. Class A, 2 mℓ volumetric flasks with hexagonal base, Fisher Scientific Company, Catalog #20814B.

15. Boekel desiccating cabinet modified for nitrogen flow, Curtin Matheson Scientific Incorporated, Catalog #076-190.

16. 6 position gas manifold for sample concentrating, Alltech Associates, Catalog #9555.

17. Zero grade nitrogen

18. Teflon Lab-Tape, Fisher Scientific Company, Catalog #14-831-300A, 13 mm width.

Analysis

1. Perkin-Elmer Model 3920B gas chromatograph equipped with a flame ionization detector.

2. Soltec Model B-281 1 mv recorder.

3. Hewlett-Packard Model 3354 GC computer system with remote teletype printout.

4. Hewlett-Packard Model 1865A A/D Converter.

5. 5 μℓ Hamilton liquid syringe, Alltech Associates, Catalog #N-75.

List of Reagents

All compounds used in sample acquisition and workup are listed in this section. Formula weights, grade of purity, manufacturer and catalog number are listed for each reagent.

1. Potassium hydroxide, KOH, formula weight = 56.11, Mallinckrodt, 85% analytical reagent grade pellets, Catalog #6984.

2. Ethyl ether, anhydrous, $(CH_3CH_2)_2O$, formula weight = 74.12, Mallinckrodt, ACS analytical reagent grade, Catalog #0848.

3. Sodium sulfate, anhydrous, Na_2SO_4, formula weight = 142.04, Mallinckrodt, ACS analytical reagent grade, granular, Catalog #8024.

4. Sulfuric acid, H_2SO_4, formula weight = 98.08, Mallinckrodt, ACS analytical reagent grade, Catalog #2876.

5. o-chlorophenol, $Cl(C_6H_4OH)$, formula weight = 128.56, Eastman Kodak Company, analytical reagent grade, Catalog #1087.

6. Phenol, C_6H_5OH, formula weight = 93.11, Mallinckrodt, ACS analytical reagent grade, loose crystals, Catalog #0028.

7. Salicylaldehyde, 2-HOC_6H_4CHO, formula weight=122.13, Eastman Kodak Company, analytical, reagent grade, Catalog #225.

8. m-cresol, $CH_3\ C_6H_4OH$, formula weight = 108.14, Aldrich Chemical Company, 99+% Gold Label, Catalog #C8,572-7.

9. p-cresol, $CH_3C_6H_4OH$, formula weight = 108.14, Aldrich Chemical Company, 99+% Gold Label, Catalog #C8,575-1.

10. p-ethylphenol (4-ethylphenol), $C_2H_5C_6H_4OH$, formula weight = 122.17, Aldrich Chemical Company, 97%, Catalog #E4,420-5.

11. 2-isopropylphenol, $(CH_3)_2\ CHC_6H_4OH$, formula weight = 136.19, Aldrich Chemical Company, 97%, Catalog #12,952-6.

12. 2,3-dimethylphenol (2,3-xylenol), $(CH_3)_2\ C_6H_3OH$, formula weight=122.17, Aldrich Chemical Company, 97%, Catalog #D17,400-9.

13. 3,5-dimethylphenol (3,5-xylenol), $(CH_3)_2\ C_6H_3OH$, formula weight = 122.17, Aldrich Chemical Company, 99.9+% zone refined, Catalog #15,085-1.

14. 2,4,6-trimethylphenol, $(CH_3)_3C_6H_2OH$, formula weight = 136.19, Aldrich Chemical Company, 99%, Catalog #T7,900-6.

15. 2,3,5-trimethylphenol, $(CH_3)_3C_6H_2OH$, formula weight = 136.19, Aldrich Chemical Company, Catalog #T7,860-3.

16. 2,3,5,6-tetramethylphenol, $(CH_3)_4\ C_6HOH$, formula weight = 150.22, Aldrich Chemical Company, 90+%, Catalog #17,877-2.

Preparation of Reagents

Absorbing solution, 1 N KOH

132.02g of KOH pellets are dissolved in deionized water in a 2000 ml volumetric flask. When the solution cools to room temperature the volume is adjusted to 2000 ml.

50% H_2SO_4

Concentrated H_2SO_4 (500 mℓ) is slowly added to 500 mℓ of chilled deionized water with swirling and shaking. The solution is stored in a glass bottle.

Internal Standard - 300 μg/mℓ o-chlorophenol

Approximately 0.0300g of o-chlorophenol is added to a 100 mℓ volumetric flask and filled to volume with ethyl ether. This solution is sealed with Teflon tape and refrigerated.

External standard stock solution

The external standard is prepared by blending the following phenols in a 1000 mℓ volumetric flask and diluting with CH_2Cl_2. This solution is sealed with Teflon tape and refrigerated.

	Wt. (mg)
Phenol	150
Salicylaldehyde	300
m-cresol	150
p-cresol	50
p-ethylphenol	100
2-isopropylphenol	150
2,3-xylenol	100
3,5-xylenol	50
2,4,6-trimethylphenol	100
2,3,5-trimethylphenol	100
2,3,5,6-tetramethylphenol	200
o-chlorophenol	300

Dilute external standard

10 mℓ of the stock external standard to diluted to 100 mℓ with CH_2Cl_2. This solution is sealed with Teflon tape.

REFERENCES

Brown, R. A., Searl, T. D., King Jr., W. H., Dietz, W. A. and Kelliher, J. M., Rapid Methods of Analysis for Trace Quantities of Polynuclear Aromatic Hydrocarbons and Phenols in Automobile Exhaust, Gasoline and Crankcase Oil, Final Report for CRC - APRAC Project CAPE-12-68, Esso Research and Engineering Company, Linden, New Jersey, 1973.

Carter, M. J. and Huston, M. T., Environ., Sci. Tech., Vol. 12, pg. 309, 1978.

Preston, S. T., A Guide to the Analysis of Phenols by Gas Chromatography, PolyScience Corporation, Niles, Illinois, 1966.

Bartle. K. D., Elstub, J., Novotny, M. and Robinson, R. J., Journal of Chromatography, Vol. 135, pg. 351, 1977.

Ma, T. S. and Speigel, D., Microchemical Journal, Vol. 10, pg. 61, 1966.

Sheffer, H. E., Perry, R. L., Thimineur, R. J., Adams, B. T., Simonian, J. L., Zutty, N. L. and Clendenning, R. A., Ind. Eng. Chem. Prod. Res. Develop., Vol. 10, pg. 362, 1971.

Yrjanheikki, Erkki, Am. Ind. Hyg. Assoc. J., Vol. 39, pg. 326, 1978.

Stanley, T. W., Sawicki, E., Johnson, H. and Pfaff, J. D., Mikrochim, Acta, Vol. 1, pg. 48, 1965.

Umbreit, G. and Houtman, R. L., Journal of Pharmaceutical Sciences, Vol. 56, pg. 349, 1967.

Lawrence, J. F., Journal of Chromatographic Science, Vol. 17, pg. 147, 1979.

Wolkoff, A. W. and Larose, R. H., Journal of Chromatography, Vol. 99, pg. 731, 1974.

Afghan, B. K., Belliveau, P. E., Larose, R. H. and Ryan, J. F., Analytica Chimica Acta, Vol. 71, pg. 355, 1974.

Mindrup, Jr., R., Industrial Research/Development, pg. 79, August, 1978.

Eichelberger, J. W., Dressman, R. C. and Longbottom, J. E., Environmental Science and Technology, Vol. 4, pg. 576, 1970.

Barber, E. D., Sawicki, E. and McPherson, S. P., Analytical Chemistry, Vol. 36, pg. 2442, 1964.

Heenan, M. P. and McCallum, N. K., Journal of Chromatographic Science, Vol. 12, pg. 89, 1974.

Crouse, R. H., Garner, J. W. and O'Neill, H. J., J. of G.C., pg. 18, February, 1963.

Kawahara, F. K., Analytical Chemistry, Vol. 40, pg. 1009, 1968.

Kushnir, I., Barr, P. A. and Chortyk, O. T., Analytical Chemistry, Vol. 42, pg. 1619, 1970.

Spears, A. W., Analytical Chemistry, Vol. 35, pg. 320, 1963.

Chriswell, C. D., Chang, R. C. and Fritz, J. S., Analytical Chemistry, Vol. 47, pg. 1325, 1975.

Braithwaite, B. and Penketh, G., Analytical Chemistry, Vol. 36, pg. 185, 1964.

Shulgin, A., Analytical Chemistry, Vol. 36, pg. 920, 1964.

Argauer, R. J., Analytical Chemistry, Vol. 40, pg. 122, 1968.

Landault, C. and Guiochen, G., Analytical Chemistry, Vol. 39, pg. 713, 1967.

Fisher, G. E. and Neerman, J. C., I and EC Product Research and Development, Vol. 5, pg. 288, 1966.

Cohen, I. C. Norcup, J., Ruzicka, H. A. and Wheals, B. B., J. Chromatog., Vol. 44, pg. 251, 1969.

Bark, L. S. and Clarke, K. F., J. Chromatog., Vol. 48, pg. 418, 1970.

Di Corcia, A., Journal of Chromatography, Vol. 80, pg. 69, 1973.

Seiber, J. N., Crosby, D. G. Fouda, H. and Soderquist, C. J., J. Chromatogr., Vol. 73, pg. 89, 1972.

APPENDIX K

SULFATE PROCEDURE

Determination of Soluble Sulfates in Automobile Exhaust by Automated HPLC Modification of the Barium Chloranilate Method

by

Silvestre B. Tejada, John E. Sigsby, Jr.
and Ronald L. Bradow
Mobile Source Emissions Research Branch
Environmental Sciences Research Laboratory

1. Principle and Applicability

1.1 Principle

Automotive exhaust is vented into a dilution tunnel where it is mixed with a flowing stream of cool filtered air. In the tunnel, the SO_3 reacts rapidly with water in the exhaust to form sulfuric acid aerosols. The aerosols are allowed to grow to filterable size range and are collected on fluorocarbon membrane filter downstream of the tunnel via isokinetic probes mounted in the following aerosol stream. Particulate sulfate salts are collected as well.

Sulfuric acid on the filter is converted to ammonium sulfate by exposure to ammonia vapor. The soluble sulfates are leached from the filter with a measured volume of 60% isopropyl alcohol - 40% water solution (60% IPA). A fixed volume of the sample extract is injected into a high pressure liquid chromatograph (HPLC) and pumped through a column of strong cation exchange resin in Ag^+ form to scrub out the halides (Cl^-, Br^-), then through a column of strong cation exchange resin in H^+ form to scrub out the cations and convert the sulfate to sulfuric acid and finally through a reactor column of barium chloranilate crystals to precipitate out barium sulfate and release the highly UV absorbing chloranilate ions. The amount of chloranilate ions released is equivalent to the sulfate in the sample and is measured by a sensitive liquid chormatograph UV detector at 310-313 nanometers. All the reactions and measurement take place in a flowing stream of 60% IPA. The scrubber and reactor columns also function as efficient filter media for any solid reaction products formed during passage of the sample through the column system.

1.2 Applicability

The method as specified is applicable to the determination of soluble sulfates in automobile exhaust. It may be used for the analysis of sulfates in samples where the sulfates can be leached out with water or aqueous IPA solution. Aqueous extracts must be made up to 60% IPA before they can be analyzed.

2. Interferences

2.1 Cationic interferences are removed by the strong cation exchange resin in H^+ form.

2.2 Halide interferences are removed by the strong cation exchange resin in Ag^+ form. Other anions which form insoluble salts with silver are also removed.

2.3 Sulfide is measured quantitatively as sulfate.

2.4 Anions which form strong acids after passage through the cation exchanger in H^+ form interfere positively. Nitrate at 60 μgs/mℓ gives an apparent sulfate response corresponding to 8 μgs/mℓ.

2.5 Presence of anionic interference is manifested by a negative peak immediately preceding the positive apparent sulfate peak.

2.6 Organics with absorption bands at 310-313 will interfere positively.

3. Range, Sensitivity and Precision

3.1 The absolute amount of $SO_4^=$ normally injected into the system is between 0 - 12.5 μgs. For a typical sample injection volume of 0.5 mℓ, this translates to a concentration working range of 0 - 25 μgs/mℓ. Working range can be extended by using a smaller sample injection volume for concentrated samples or conversely, by using a larger injection volume for dilute samples.

3.2 Minimum detectable quantity of $SO_4^=$ is in the low nanogram range. There are commercially available liquid chromatograph UV detectors capable of detecting 5 nanograms of sulfate at a signal to noise ratio of about 5. Figure 1 shows typical recorder response for a 0.5 mℓ injection of sulfate samples at trace concentration levels (0.01 - 0.1 μgs/mℓ.

3.3 Precision better than 3% at 0.5 μg/mℓ $SO_4^=$ level and better than 2% between 1 and 20 μgs/mℓ for four repetitive runs have been attained. Table 1 and Figure 2 show typical reproducibility obtained with the automated BCA system.

4. Apparatus

A schematic of the principal components of the automated BCA set up is shown in Figure 3.

4.1 Hardware

4.1.1 Basic System

4.1.1.1 High pressure liquid chromatograph pump (LP). The pump must be capable of delivering liquids at flow rates of at least 3 mℓ/min at pressures as high as 1200 psi. Liquid pumps capable of delivering pulseless and constant liquid flow are recommended for good quantitation. Most HPLC pumps in the market are adequate.

4.1.1.2 UV detector (D) equipped with low dead volume (8 µℓ) flow-through cell and a grating, prism or appropriate interference filter to isolate a narrow radiation band centered at 310-313 nanometers. For low noise and long life, a UV detector equipped with low pressure mercury lamp and a 313 nanometer narrow band pass interference filter is recommended.

4.1.1.3 A two position, six port, high pressure, low dead volume sample injection valve (SV). This must be equipped with interchangeable external loop (L). Two loop sizes are desirable: a 0.5 mℓ volume for the 0 - 20 µg/mℓ range and a 100 µℓ volume for 0 - 100 µgs/mℓ. range. The sample valve must be equipped with an external handle for manual operation or an air actuator for remote and/or automatic operation. These valves are commercially available and have pressure ratings as high as 7000 psi.

4.1.1.4 Recorder. Must be multi-range, with chart speed as low as 10 minutes per inch. Dual channel is preferable so that chromatogram can be simultaneously recorded at two different sensitivities.

4.1.1.5 Strong cation exchange resin column (CX-Ag^+), 4 mm I.D. by 1/4 inch O.D. by 6 inches long stainless steel column packed with chromatographic grade, strongly acidic cation exchange resin in silver (Ag^+) form.

4.1.1.6 Strong cation exchange resin column (CX-H^+), 4 mm I.D. by 1/4 inch O.D. by 9 inches long, stainless steel column packed with strongly acidic cation exchange resin in hydrogen (H^+) form.

4.1.1.7 Barium chloranilate column (BCA), 4 mm I.D. by 1/4 inch by 1 inch long stainless steel column packed with crystalline barium chloranilate.

4.1.1.8 1/4" to 1/16" stainless steel reducer preferably fitted with 5 micron pore size frit - for column inlet and end fittings.

4.1.1.9 1/4" to 1/4" stainless steel unions.

4.1.1.10 1/16" to 1/16" low dead volume stainless steel couplings to interconnect CX-Ag^+ to CX-H^+ to BCA columns.

4.1.1.11 1/4" and 1/16" nuts and ferrules.

4.1.1.12 Reservoir (LR) for the solvent (60% IPA).

4.1.2 Options - These items are needed for automating the basic system.

4.1.2.1 Integrator, for measuring peak areas. Recommended unit must have baseline tracking capability and possibly with built-in calculation accessory. The integrator extends useful dynamic range of detector response for a given sample loop size beyond that of the strip chart recorder.

4.1.2.2 Peristaltic pump, (PP), to draw sample from its container and load it into sample loop. Silicone pump tubing is recommended.

4.1.2.3 Automatic sampler (AS), available from commercial sources. This is needed if the number of samples to be analyzed is large and manpower is limited.

4.1.2.4 Three timer relays to control pump, sampler, injection valve and integrator and provide automatic reset for cyclic operations.

4.1.2.5 Prepackaged sampler systems for HPLC application are commercially available.

5. Principle of Operation

Solvent (60% IPA) in reservoir LR (Figure 3) is continuously pumped by an HPLC LP through a column of strong cation exchange resin in silver form, $CX\text{-}Ag^+$, then through a column of strong cation exchange resin in hydrogen form, $CX\text{-}H^+$, then through a reactor column of barium chloranilate, BCA, and finally through a flow-through cell of a UV detector, D, and on to waste. $CX\text{-}AG^+$ removes the halides (Cl^-, Br^-, F^-) and other anions which precipitate with silver; $CX\text{-}H^+$ removes metallic cations and converts the sulfate to sulfuric acid, and the BCA reacts with the sulfate to form barium sulfate precipitate and a soluble UV absorbing dye, chloranilic acid and its ions. Background absorbance at 310-313 nanometers is continuously measured and monitored on a strip chart recorder.

Sample is introduced into the system without flow interruption by means of a two-way six port low dead volume sample injection valve SV. In load position "A" (see Figure 3) the peristaltic pump, PP, draws the sample from a cuvette in the automatic sampler AS and pumps it into port 4 filling external sample loop L then through port 5 to waste. (Sample loop loading may also be accomplished by pushing the sample through port 4 by means of a syringe.) The high pressure liquid flow comes in through port 1, bypasses the loop L, comes out of port 2, and continues on through the three columns and the flow-through cell of the UV detector D and on to waste.

After loop L is loaded with sample, injection valve SV switches to inject position "B". The high pressure stream purges the loop and pushes the sample through the cation exchangers and then through the BCA column where the color reaction takes place. The $BaSO_4$ precipitate is retained in the column while the acid chloranilate is carried by the flowing liquid through the detector system for colorimetric measurement.

6. Apparatus

6.1 Pipette, volumetric, 1, 2, 4, 5, 8, 25, 50, 100 mℓ

6.2 Pipette, measuring, 1, 2, 5, 10 mℓ

6.3 Automatic burette, 25 mℓ

6.4 Volumetric flasks, 10, 25, 50, 100, 500, 1000, 2000 mℓ

6.5 Bottles, polypropylene, with screw caps, 30, 60, 125, 250, 500, 1000

6.6 Microbalance

6.7 Vortex test tube mixer

6.8 Centrifuge

6.9 Magnetic mixer

6.10 Magnetic bars

6.11 Graduated cylinders

6.12 Automatic dispenser pipet, 5, 10, 20 mℓ (optional)

6.13 Automatic burette, 10 mℓ (motor driven, optional)

6.14 Ammoniation chamber (Figure 5)

7. Reagents

7.1 Isopropyl alcohol (IPA), spectro quality grade or equivalent

7.2 Water, doubly deionized, distilled.

7.3 60% IPA. Add 4 parts water to 6 parts IPA by volume. Store in tightly capped bottles.

7.4 Barium chloranilate, suitable for sulfate analysis. Must be crystalline, granular, preferably with average granule length of about 200 microns. Finer particles cause excessive column pressure drop.

7.5 Cation exchange resin, chromatographic grade, strongly acidic, hydrogen form, 100 - 200 mesh.

7.6 Hydrochloric acid (4N). Add 30 mℓ concentrated hydrochloric acid to 60 mℓ of deionized water.

7.7 Ammonium sulfate, primary standard

7.8 Silver nitrate (1N). Dissolve 17 grams silver nitrate in deionized water and make up to 100 mℓ. Store in the dark in an amber colored reagent bottle.

8. Procedure

8.1 Column Preparation

8.1.1 Barium chloranilate column. In order to prepare a full column with minimum dead volume, connect two lengths of 4 mm I.D., 1/4" O.D. stainless steel tubing as shown in Figure 4 with a = 1", b = 2". Connect a small funnel to open end of B with a flexible tubing sleeve. Fill the funnel halfway with barium chloranilate and thump the tube several times or use a vibrator (i.e., electric pencil engraver) to pack the solid in the column. Continue the operation until B is completely filled. Remove the funnel and cap the open end of B with a 1/4" to 1/16" reducer fitted with 5 micron stainless steel frit. The 5 micron stainless steel frit in column A may be replaced with a stainless steel wire screen with nominal porosity of 10 microns. Connect B to the HPLC pump, connect a flexible tubing at A and direct the tubing to waste reservoir. Fill HPLC pump reservoir with 60% IPA. Activate HPLC pump according to manufacturer's instructions, set flow at 3 - 4 mℓ/min and let solvent flow for at least 20 minutes. This procedure removes the fines which can cause background drift and at the same time compresses the barium chloranilate crystals to fill the dead volume in column A. Deactivate the HPLC pump, disconnect the composite column from the pump, then column A from the composite column. Connect a 1/4" to 1/16" reducer fitted with 5 micron frit to open end of A.

8.1.2 Cation exchange resin columns

8.1.2.1 Cation exchange resin hydrogen form. Add strongly acidic cation exchange resin, 100 - 200 mesh, to 160 mℓ of 4 N HCl in a 250 mℓ Erlenmeyer flask until a wet volume equivalent to 40 mℓ has settled at the bottom. Soak for at least 3 hours with occasional stirring with a glass rod. Decant the acid, add 100 mℓ deionized water, stir and decant the liquid as soon as most of the solids have settled at the bottom. This procedure removes most of the fines. Repeat rinsing procedure several times until the rinse liquid gives neutral reaction to pH paper. Transfer half of the resin to a 150 mℓ Erlenmeyer flask for conversion to the silver form.

Connect two sections of 1/4" O.D., 4 mm I.D. stainless steel tubing as in 8.1.1 with a = 9 and b = 5. The reducer on the outlet end of A should have a 5 micron stainless steel filter frit. These frits are available commercially. The fritt must be able to withstand high pressure (1200 psi). (If the cation exchange resin breaks through the frit and comes to contact with the barium chloranilate column, the column gets plugged.) Connect a small funnel to open end of B with a flexible tubing sleeve. Clamp composite column vertically and connect open end of A to vacuum line equipped with liquid trap.

Fill funnel with deionized water and turn vacuum slowly so that the column is completely filled with water. Add enough water so that water level is in the funnel cone; stop the vacuum and add the slurry of freshly washed resin (H^+ form). Let the resin settle by gravity until the resin top is halfway in the funnel stem. Open the vacuum slowly and keep adding the resin slurry until the composite column is completely filled. Proceed as in 8.1.1 beginning with the sentence "Remove funnel and cap open end of B...".

8.1.2.2 Cation exchange resin, silver form. Add 60 mℓ of 1 N $AgNO_3$ solution to the other half of the washed cation exchange resin, hydrogen form, in a 150 mℓ Erlenmeyer flask. Stir with a glass rod, cover the the flask with aluminum foil and soak the resin overnight.

Decant the $AgNO_3$ solution into a waste reservoir. Add 100 mℓ deionized water, stir and decant the liquid as soon as most of the resins have settled at the bottom. Repeat the rinsing procedure until the rinse liquid remains clear when treated with a few drops of 4 N HCl.

Connect two sections of 1/4" O.D., 4 mm I.D. stainless steel tubing as in 8.1.1 with a = 6" and b = 5". Load the column following the procedure described in section 8.1.2.1.

8.2 Priming System for Analytical Run

Connect outlet end of cation exchange resin (Ag^+ form) column to inlet end of cation exchange resin (H^+ form) column with a low dead volume 1/16" to 1/16" stainless steel tubing connector. Similarily connect the outlet end of the second column to the barium chloranilate column. Plumb the composite column to the automated set up as shown in Figure 3. Fill solvent reservoir LR with 60% IPA, activate the HPLC pump, detector, recorder, sample injection valve, sampler and peristaltic pump. During this initial operation dip the samplling probe in 100 mℓ of 60% IPA. Set the liquid flow rate at 3 mℓ/min. (Flow rate is conveniently measured by directing the effluent from the UV detector to a microburette and measuring the time in seconds needed to fill a volume of 3 mℓ.) Let run for at least 30 minutes. Deactivate sample injection valve, sampler and peristaltic pump. Leave other components in operating mode. When absorbance background is stable at the appropriate sensitivity setting of the detector, the system is ready to analyze sulfate samples.

8.3 Preparation of Standards

Sulfuric acid, sodium sulfate or ammonium sulfate may be used as standards. Ammonium sulfate is preferred.

8.3.1 $SO_4^=$ (100 μgs/mℓ) standard, alcoholic stock solution. Dissolve 275000 ± 100 μgs of primary standard ammonium sulfate in 200 mℓ of deionized water in a 2000 mℓ volumetric flask. Add 300 mℓ pure IPA, shake vigorously until thoroughly mixed, and make up to volume with 60% IPA. Store in clean polypropylene bottles. (Note: a. There is a volume decrease of about 2.7% when two parts of water is mixed with 3 parts of IPA. b. Do not use detergents nor dichromate-sulfuric acid solution for cleaning glasswares. Sulfate background from these sources are difficult to remove. 50% (v/v) nitric acid/water is preferable.) Prepare from this stock solution $SO_4^=$ calibration standards (0.5 to 20 µgs/mℓ) by dilution of appropriate aliquots with 60% IPA. Store standards in capped polypropylene bottles.

8.3.2 $SO_4^=$ (100 µgs/mℓ) standard, aqueous stock solution. Dissolve 275000 ± 100 µgs of primary standard ammonium sulfate in 200 mℓ of deionized water in a 2000 mℓ volumetric flask and make up to volume with deionized water. Store in polypropylene bottle.

8.3.3 Alternative method of preparing calibration standards. Use a repetitive dispenser, burette or automatic syringe pump. Using either the alcoholic or aqueous $SO_4^=$ (100 µgs/mℓ) stock solution dispense appropriate volumes containing 10, 20, 40 ..., 180, 200 µgs of $SO_4^=$ into 30 of 60 mℓ polypropylene bottles. Prepare 10 for each sulfate level. Evaporate the liquids completely by placing the bottles uncapped in an oven maintained at 80 - 100°C. Cool, cap the bottles and store until ready to use. These solid standards can then be extracted in the same manner as the filter samples.

8.4 Ammonia Treatment of Filter Samples

This treatment converts sulfuric acid particulate into ammonium sulfate. Conversion of ammonium salt was observed to improve precision of sulfate measurement. Sample losses from accidental contact of the filter surface with another sufrace is minimized. An additional advantage is that the sulfate is converted to the same form as the calibration standard.

Figure 5 shows a simple schematic of an ammoniation set-up. Filter samples on open Petri dishes are placed face up on perforated shelves of the ammoniation box. The box is evacuated, valve V_1 is closed, and valve V_2 is opened. Ammonia from concentrated ammonium hydroxide fills the box and converts sulfuric acid to ammonium sulfate. One hour exposure to ammonia vapor is adequate. V_2 is closed, most of the ammonia is pumped out and passed through a KH_2PO_4 scrubber column. Vacuum is released by switching V_1 to vent.

8.5 Extraction of Soluble Sulfates

It is important that the water/IPA ratio in the sample and in the mobile phase be the same. A sample richer in water content than the mobile phase will momentarily increase the solubility of barium chloranilate and will produce a positive peak above a flat background; that richer in IPA will produce a negative peak. Variations will occur if the solvent used in the preparation of the standards and in the extraction of the filter samples were taken from a different stock as that used in the mobile phase. Therefore, it is strongly recommended that the extraction solvent be taken from the same stock solution as the mobile phase or, if possible, directly from the liquid reservoir of the HPLC pump. The use of solid standards as prepared in 8.3.3 will eliminate variability due to IPA/water mismatch.

8.5.1 From Fluorocarbon Membrane Filters

Place filter in appropriate size polypropylene bottle. If approximate sulfate level is known from previous analysis of similar samples, measure adequate volume of 60% IPA to give sulfate concentration of about 10 μgs/mℓ. Otherwise add 10 mℓ 60% IPA and cap the bottle tightly. As a rule of thumb, the sulfates constitute about 40 - 50% of the total particulate mass if most of the particulates on the filter is sulfuric acid. Such cases are generally encountered with filter samples from catalyst equipped cars run on non-leaded fuels. Particulate mass loading of a filter is an important piece of information in deciding appropriate volumes of extracting solution to use.

Shake the bottle vigorously until the filter callapses and is completely immersed in the solvent. A vortex test tube mixer is recommended. Twenty seconds shaking with a vortex test tube mixer is adequate to leach the soluble sulfates from the filter. If there are no visible suspended particulates, the clear solution can be used directly for analysis. If suspended carbon or other particles are apparent, filter about 5 mℓ of the extract by using a syringe with a μ pore size fluorocarbon in-line filter. These filter syringes are available commercially. If the particles are sufficiently large, they can be removed from the bulk solution by centrifugation.

8.5.2 From glass fiber filters

This procedure is for the extraction of 47 mm diameter filters. Adjust the volume of the extracting solvent accordingly for different size filters.

Place the filter in appropriate size polypropylene bottle. If approximate $SO_4^=$ level is known, add adequate volume of 60% IPA to give sulfate concentration of about 10 μgs/mℓ. Otherwise, add 30 mℓ 60% IPA and cap bottle tightly. Shake with a vortex mixer until the glass fibers disintegrate. Where large solvent volume and inordinately long shaking time are required, stirring with a Teflon clad magnetic stirring bar is preferable. Glass fibers are easily separated from the bulk liquid by using a centrifuge. If finely suspended particles are present, as in the case of diesel and some non-catalyst exhaust samples, syringe filtration as mentioned in 8.5.1 must be used. In some cases a 0.2 μ pore size filter is necessary.

8.6 Water extracts

Water extracts of filter samples may also be analyzed by the automated BCA method. One important requirement, however, is that the solution must be made up to 60% IPA (e.g., 4 parts of the extract must be added to 6 parts of pure IPA, v/v) before the sample can be analyzed. If the water extract is mixed directly with pure IPA, volume shrinkage (about 2.7%) must be taken into account in the calculation of concentration.

Another approach is to evaporate completely the solvent in a known volume of the extract in polypropylene bottle similar to the preparation of solid calibration standard in 8.3.3. The residue may be ammoniated in the plastic bottle as in 8.4 and extracted as in 8.5.1 or 8.5.2.

8.7 Analysis

Set instrument in operating mode, remove sample probe from the holder and dip in 100 mℓ 60% IPA. Adjust the flow rate in 3 mℓ/min, allow the instrument to cycle several times until a stable background is obtained, then remount sample probe to holder. Adjust loading time or peristaltic pump rate so that at least twice the volume of the sample as the volume of the sample injection loop has exited the waste port of the sample injection valve. Adjust sample injection time so that peaks from successive sample injections do not overlap. Fill sample cuvetted with samples and rinse solution (60% IPA) and place according to a sampling pattern, blank, sample, blank, sample, blank... The rinse solution (blank) is necessary to ascertain that there is no memory effect from previous sample injection.

A series of at least 6 calibration standards spanning the concentration range of interest is run before samples are run. A control standard may be placed every 10 samples as a quality check on the stability of the system. Dilution may be necessary if the sample peak height is beyond the range of the calibration standard. If a large number of samples needs dilution, it may be more convenient to merely change the size of the sample loop.

Plot peak height (or area if an integrator is also used) vs concentration in μgs/mℓ of the sulfate standard. The curve is not linear. Alternatively, the peak height or area concentration data may be fitted into a polynomial of the form:

$$y = a_0 + a_1 + a_2x^2 + a_3x^3 + a_4x^4 + \ldots$$

where: y = sulfate concentration in μgs/mℓ

x = peak height or area

8.8 Calculations

Calculate the concentration of sulfate as μgs $SO_4^=$/mℓ using the calibration curve or the polynomial regression equation. Total soluble sulfate $(SO_4^=)_F$ in the filter is then given by:

$$(SO_4^=)_F = (SO_4^=)_d \times V_o \times d$$

where: V_o = total volume in mℓ of original sample extract

$(SO_4^-)_d$ = sulfate concentration of the diluted sample in μgs/mℓ d = dilution factor

= 1, if there is no dilution of the extract before analysis

= V_a/V_d

V_a = aliquot volume in mℓ of sample diluted with 60% IPA

V_d = final volume in mℓ of the aliquot sample after dilution with 60% IPA

Example:

Suppose 10 mℓ of 60% IPA was used to extract the soluble sulfated in the filter and that 2 mℓ of this was further diluted with 4 mℓ 60% IPA to bring detector response within calibration range. Suppose that the concentration of the diluted sample was found to be 5 μgs/mℓ . Then,

$(SO_4^=)_d$ = 5 μgs/mℓ

V_o = 10 mℓ

V_a = 2 mℓ

V_d = 2 + 4

= 6 mℓ

$(SO_4^=)_F$ = 5 x 10 x (6/2)

= 150 μgs

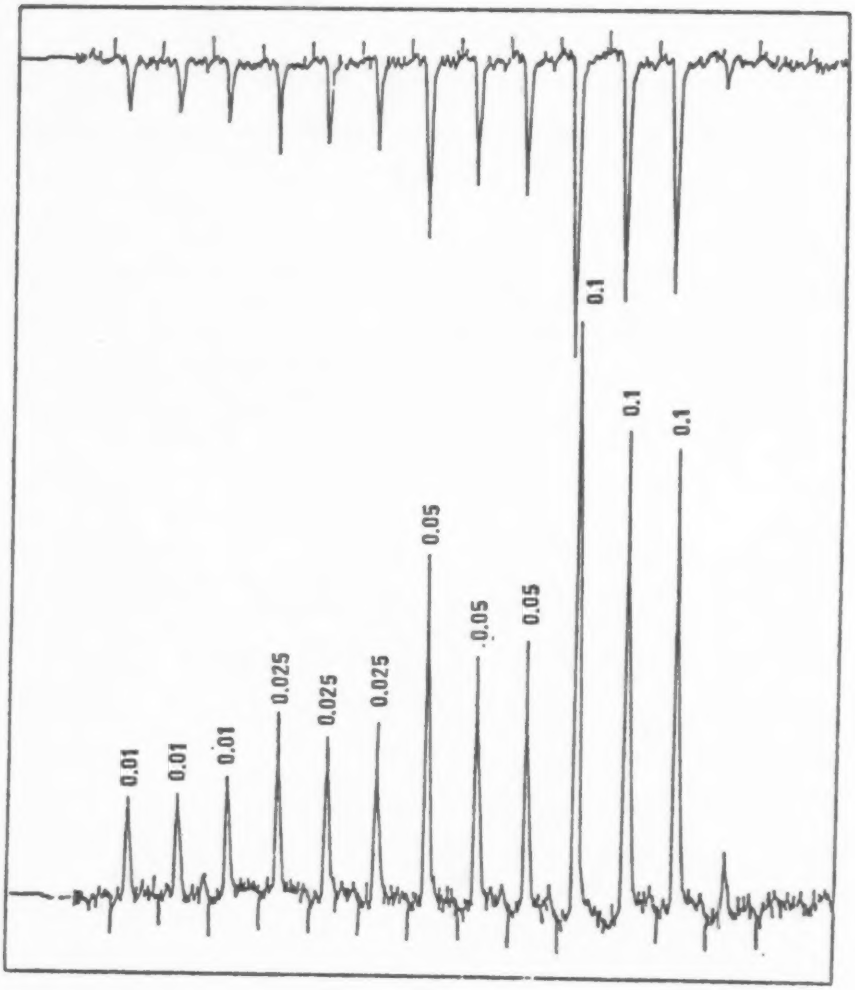


Figure 1. Chromatogram at trace sulfate levels, 0.01, 0.02, 0.05, 0.01 μgs $SO_4^=$/mℓ. Flow rate at 3.2 mℓ/min. Detector sensitivity at 0.01 absorbance units full scale. Sample volume injected = 0.5 mℓ

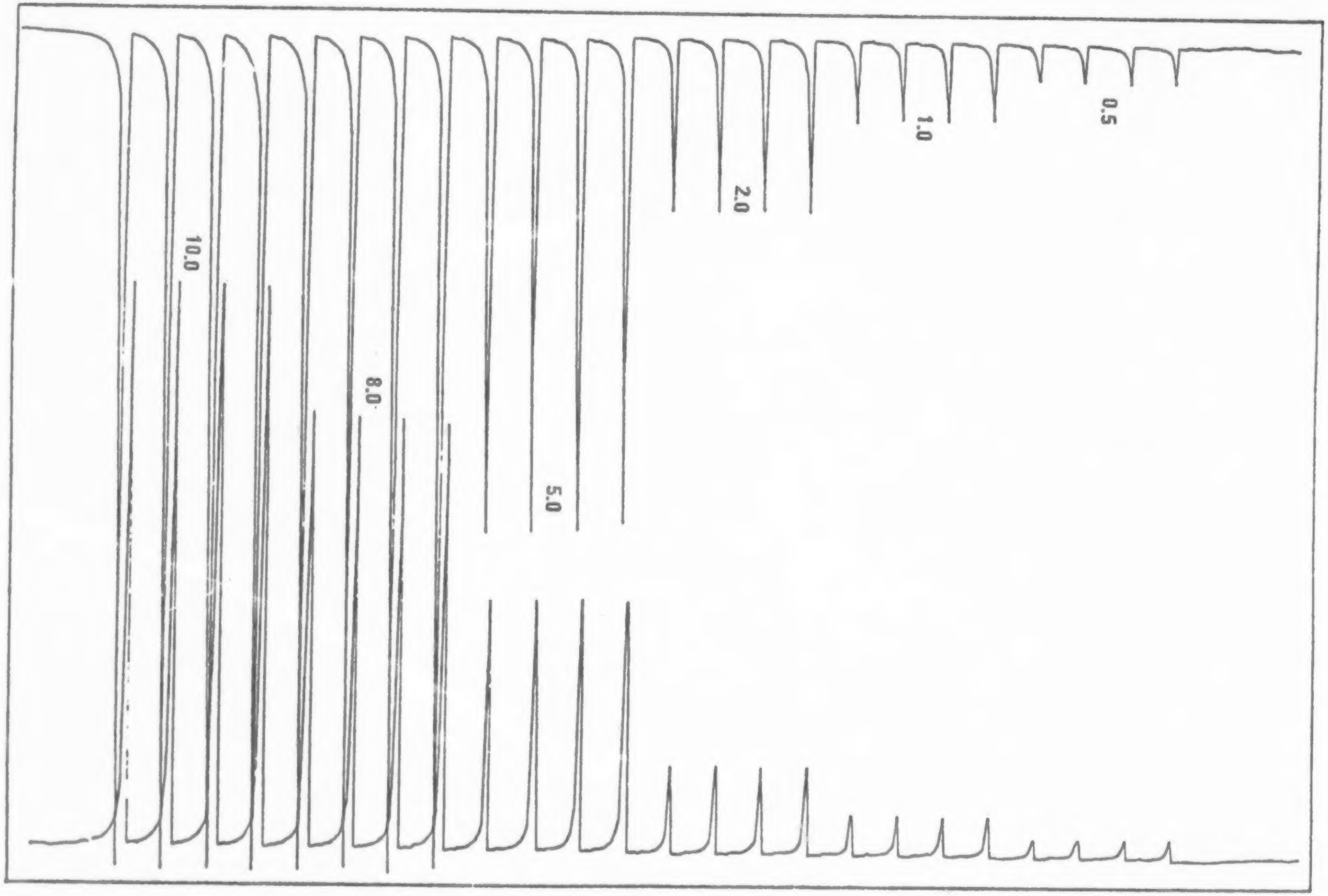
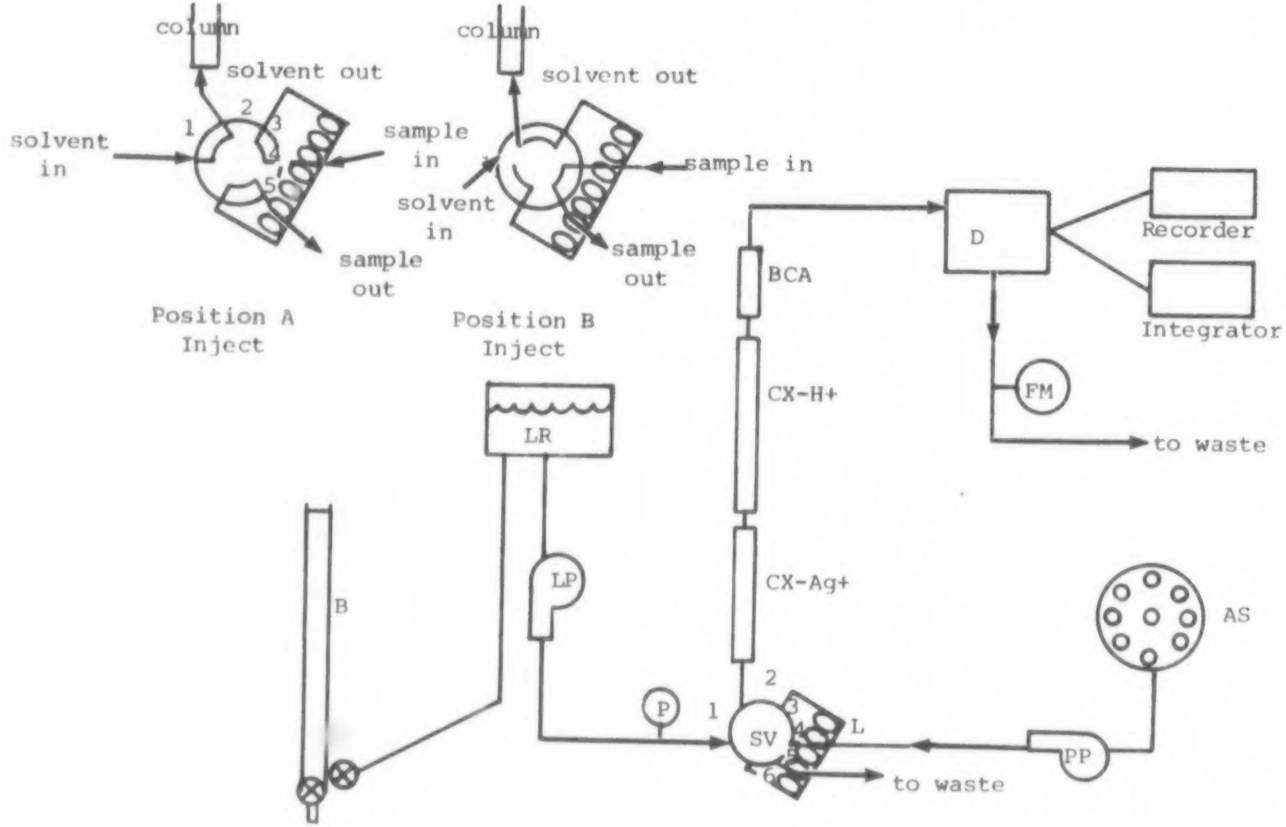


Figure 2. Reproducibility of repetitive sample injections. Flow at 3.2 mℓ/min. Detector sensitivity at 0.5 AUFS. Sample volume injected = 0.5 mℓ. Numbers above peaks are sulfate concentrations in μgs/mℓ.


column
solvent out
solvent in
1
2
3
4
5
sample in
sample out
Position A Inject
column
solvent out
sample in
solvent in
sample out
Position B Inject
LR
LP
B
P
1
2
3
4
5
6
SV
L
to waste
BCA
CX-H+
CX-Ag+
D
Recorder
Integrator
FM
to waste
AS
PP

B - buret
LR - liquid reservoir
LP - PHLC pump
P - Pressure Monitor
SV - Sample Injection valve
L - Sample loop

CX-Ag+ - Cation exchange resin, silver form
CX-H+ - Cation exchange resin, hydrogen form
BCA - Barium chloranilate
D - UV detector
FM - Flow monitor
PP - Peristaltic pump
AS - Automated sampler

Figure 3. Schematic of an automated BCA sulfate set-up.

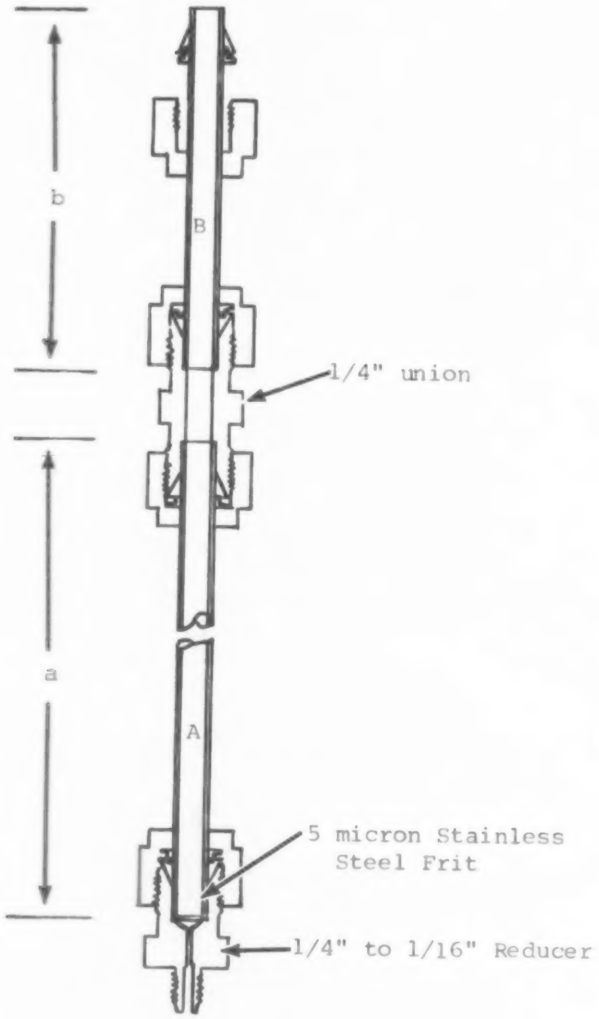

b
B
1/4" union
a
A
5 micron Stainless Steel Frit
1/4" to 1/16" Reducer

Figure 4. Configuration for packing column.

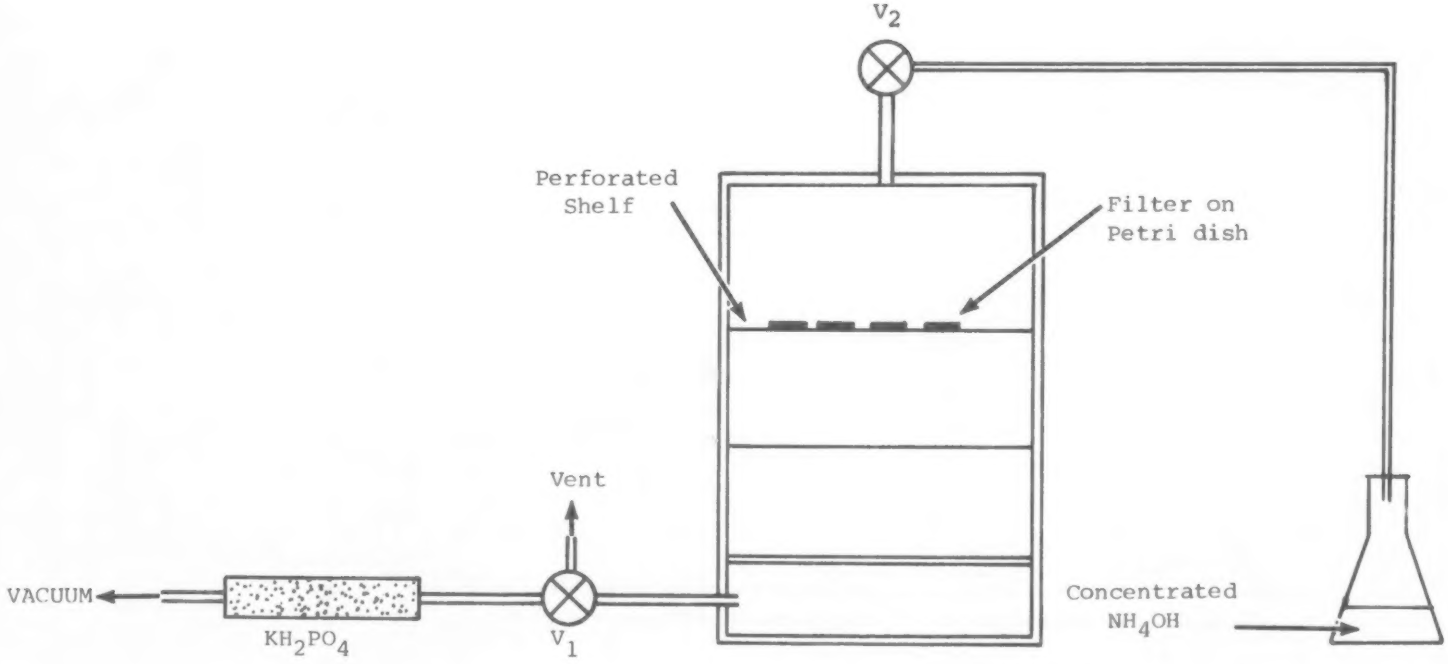

V_2
Perforated Shelf
Filter on Petri dish
Vent
VACUUM
KH_2PO_4
V_1
Concentrated NH_4OH

Figure 5. Schematic of an ammoniation set-up.

DISCREPANCIES BETWEEN EPA AND DEPARTMENT OF EMISSIONS RESEARCH BCA SULFATE PROCEDURE

4.1.1.1 - Bottled N_2 gas is used to drive 60% IPA from a reservior through the HPLC system at average rate of 4.5 mℓ/min.

4.1.1.2 - The Dupont 837 sample cell volume is 6.3 μℓ.

4.1.1.3 - A dedicated 1 mℓ sample loop is used on a manually-operated sample injection valve.

4.1.1.4 - Recorder is dual channel, 10 mv full scale, with variable chart speed set at 0.75 in/min. Only one recorder channel us used since chromatogram sensitivity is controlled at range switch on spectrophotometer.

4.1.1.6 - A 6-inch long cation column is used.

4.1.1.7 - A 2-1/2 inch long BCA column is used.

4.1.1.10 - One-quarter inch unions are used.

4.1.2 - Non-automated system is used.

6.5 - Polypropylene bottles (30 mℓ) are used for extraction of filters in 60% IPA solution.

6.8 - We don't use centrifuge.

7.2 - We use deionized water checked with $AgNO_3$ for dissolved salts.

7.3 - We store in a 5-gallon stoppered glass bottle with dispenser.

7.7 - Ours is ACS reagent, oven dried, and stored over silica gel in a dessicator.

8.3.1 - Stock and calibration standards are stored in glass bottles.

8.3.2 - Standard solution stored in glass bottles.

8.3.3 - We don't use alternative method of preparing calibration standards.

8.4 - The chamber containing sample filters in open Petri dishes is purged with ammonia from concentrated ammonium hydroxide which is then vented out via hood. The chamber is purged for 3 minutes and then the filters are isolated in the ammonia-filled chamber for one hour before their extraction in 60% IPA.

8.5.2 - We do not use glass filters for sulfate analysis.

8.6 - We do not do water extracts.

8.7 - Used in automated system only.

VALIDATION WORK AT SwRI

1. Diesel fuel gives a positive interference

    a. 1 μg diesel fuel gives response equal to 0.02 μg SO_4^{2-}.

    b. Response to diesel fuel occurs with or without BCA column in system indicating a nonsulfate interference in the fuel.

    c. Diesel fuel response can be removed by washing diesel fuel doped filter with 25 mℓ cyclohexane.

    d. Sulfate response unchanged by washing sulfate doped filter with 25 mℓ cyclohexane.

2. 5-20 percent of the sulfate response on some filters collected from diesel fuel engines was not due to sulfate.

    a. Filters washed with 25 mℓ cyclohexane were 13-20 percent lower in apparent sulfate response than unwashed filters. These filters were duplicates collected from diesel powered vehicles. Cyclohexane does not remove sulfate from sulfate doped filters. Cyclohexane does remove diesel interference from diesel doped filters.

    b. Diesel filter samples run without BCA column in analysis system were 5-18 percent lower in apparent sulfate response than identical samples run with the BCA column in place.*

* System designed to run with and without BCA column in system was similar to the system described by N. J. Khatri, J. H. Johnson and D. G. Leddy in "The Characterization of the Hydrocarbon and Sulfate Fractions of Diesel Particulate Matter," SAE Paper No. 780111, February-March, 1978. In this work they found a large portion of the sulfate due to what they attributed to hydrocarbon interferences.

APPENDIX L

DMNA SAMPLING PROCEDURE

DESIGN AND CALIBRATION OF SECONDARY DILUTER

A secondary diluter, to be used in conjuction with a constant volume sampler, has been constructed. The secondary diluter was constructed:

1. to determine the concentration of N-nitrosodimethylamine in automobile exhaust

2. to determine the composition of condensable organic vapors in automobile exhaust. Condensable organic vapors are those having molecular weights from about 140 to 300 atomic mass units.

Factors which had to be taken into consideration for construction of the secondary diluter were:

1. a proportional sample of automobile exhaust is needed

2. high levels of nitric oxide must be avoided because:

    a. NO + amine → nitrosamine artifact, which would interfere with the detection of N-nitrosodimethylamine.

    b. the oxidation of NO to NO_2 with materials in the system and on the traps would cause interference.

3. the sample must be presented to the Tenax GC trap at an appropriate flow rate and temperature so that collection is efficient and materials are not driven off the trap. (We sample at 1.6 ℓ/min and 60°C).

The design criterion was to avoid oxidation of NO_x and have a sample of 5 ppm or less of NO_x, which was accomplished by using dry nitrogen to dilute the automobile exhaust at 25:1. (Our dilution is 16.7:1.)

The secondary diluter is shown schematically in Figure 1 and its operating principels given below:

1. diluted automobile exhaust is pulled into the secondary diluter through a 1/8" OD stainless steel tube at a flow rate of approximately 2.5 ℓ/min; this flow is dependent upon the downstream pressure drop.

2. Dry nitrogen for secondary dilution is added through a roots meter and rotometer, in series, at approximately 68 ℓ/min. This flow is independent of the downstream pressure drop. (We run at 55 ℓ/min.)

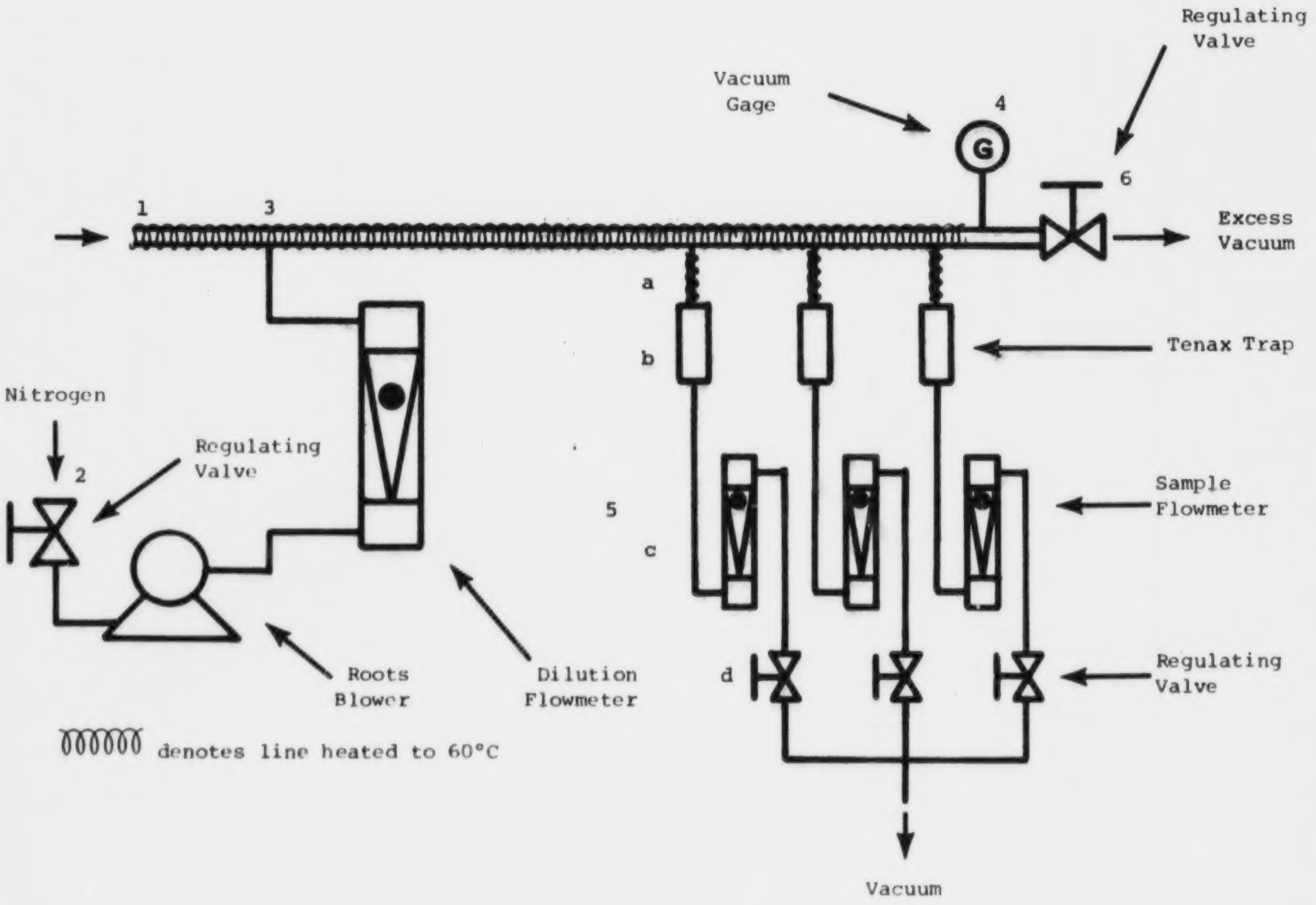

Regulating
Valve
Vacuum
Gage
4
G
6
1
3
Excess
Vacuum
a
b
Tenax Trap
Nitrogen
2
Regulating
Valve
5
c
Sample
Flowmeter
d
Regulating
Valve
Roots
Blower
Dilution
Flowmeter
denotes line heated to 60°C
Vacuum

Figure 1. Secondary diluter

3. Diluted automobile exhaust and dry nitrogen are mixed at this point and pulled through a 3/8" OD stainless steel tube 13" long.

4. A magnehelic gauge is used to monitor the pressure drop across the diluter. The reference side of the magnehelic is connected to the primary dilution tube; this allows dilution ratios to be determined without making corrections for differences in atmospheric and primary dilution tube pressure.

5. Three simultaneous samples are pulled through; (a) glass fiber filters, (b) Tenax GC traps, (c) rotometers, and (d) needle valves. The needle valves are set to maintain a flow of 2.5 ℓ/min through each sample trap. (We use Fluoropore filters and sample at 1.6 ℓ/min.)

6. Excess flow is discharged from the diluter through a needle valve, which is used to maintain the proper pressure drop across the diluter.

During the operation, it is suggested that the inlet rotometer (2) be maintained at 80 and the magnehelic gauge, (4) be maintained at 10" water, which will give dilution ratio of 25:1. These gauges should be checked every five minutes to be sure that these flows do not change. (Our rotometer is set at 65 and the magnehelic at 25" water for a dilution ratio of 16.7:1.)

CALIBRATION

The rotometers for the secondary diluter were calibrated by using a roots meter and dry test meter.

The secondary diluter was calibrated by several different, but similar experiments. The purpose of these experiments was to calibrate the dilution ratio against diluter pressure drop. Each experiment involved measuring dilution ratios obtained at various constant diluter, pressure drops as measured by the magnehelic gauge.

It was found early in the experiments that a constant source of vacuum is needed in order to maintain a steady pressure drop across the diluter.

The experiments were conducted as follows:

1. A sample of propane span gas was placed in a large empty Tedlar bag; the concentration of propane in the bag was determined by analyzing the contents of the bag on a hydrocarbon analyzer.

   One sample rotometer (5) was disconnected from its normal vacuum source and replaced by a diaphram pump of sufficient size to pull 2.5 ℓ/min. The reference side of the magnehelic was left open to atmospheric pressure, a correction for this was made for this calculating the data. The rest of the system was up as it would be for normal operation. The bag of propane span gas was connected to the sample inlet (3). The diluted sample was then collected in an emply Tedlar bag downstream of the diaphragm pump. This bag was then analyzed on a hydrocarbon analyzer and its concentration determined. By dividing the concentration of hydrocarbon in the span gas by the concentration found in the bag of diluted span gas, the dilution ratios were found for different magnehelic gauge readings.

2. The diluter was then set up as it normally will be used, except that one rotometer (5) was still connected to the diaphragm pump. A cylinder of span gas containing propane, carbon monoxide and carbon dioxide was then metered into the primary dilution tube. A sample of this diluter span gas was collected in bags on the primary diluter and at the same time bags were collected on the secondary diluter. The bags collected on both primary and secondary diluters were then analyzed on appropriate analyzers. By dividing the concentration found in the primary bag by the concentration found in the bag of diluted span gas, the dilution ratios were found for different magnehelic gauge readings.

3. The diluter was set up as it would be for making a normal test, with the exception that a rotometer was attached to the sample inlet (1). Ambient air was pulled through this rotometer while the rest of the diluter was under normal operation. By making corrections for pressure drop in the diluter, the flow of dry nitrogen into the diluter can be divided by the flow of ambient air into the diluter, giving dilution ratios for different magnehlic gauge readings. The expression used for correcting the pressure drop is $\frac{P_1V_1}{P_2} = V_2$ where:

P_1 = initial pressure
V_1 = initial volume
P_2 = final pressure
V_2 = final volume

A correction for temperature was not made because the temperature was stable at approximately 20°C and thought this difference would be of little consequence.

The dilution ratios determined by these three different experiments were plotted against differential pressures measured by the magnehlic gauge using the general expression for flow in pipe:

$$AP = \frac{2\ f'\ell}{VGD} V_2 \text{ (ref. 1)}$$

where: AP = differential pressure
f' = friction
L/D = length/diameter ratio
g = gravitational constant
v = specific volume of gas, 1/density
V = linear velocity

Since the sample inlet is of constant cross section, the linear velocity is proportional to the volumetric flow rate. In any given set of experiments, all variables in this equation other than velocity and pressure are constant. Because of this, the equation reduced to:

$$\Delta P = CV^2 = CQ^2$$

where $Q = \dfrac{\text{sample flow rate}}{\text{volumetric}}$

The dilution ratio, R, is given by:

$$R = \frac{Q_{N2} + O_s}{Q_s}$$

If $Q_s \sim Q_{N2}$, then $R = \dfrac{Q_{N2}}{Q_s}$; $Q_s = \dfrac{Q_{N2}}{R} = \dfrac{\text{Constant}}{R}$

Therefore: $\dfrac{1}{R} = C'' \sqrt{\Delta P}$

and the plot of the reciprocal of the dilution ratio against $\sqrt{\Delta P}$ should be a straight line.

Figure 2 presents all the raw data gathered in these calibrations and plotted on this basis. A linear least squares fit for these data is also presented in Figure 2. A single equation was found to adequately represent the shole date base:

$$1/R = 0.01858 \sqrt{\Delta P}\ 0.02133$$

$$r^2 = 0.9819$$

standard error of estimate = 3 percent of mean value

Reference 1. Mark's Standard Handbook for Mechanical Engineers, 7th Edition, McGraw-Hill, N.Y. (1967), p.4-66.

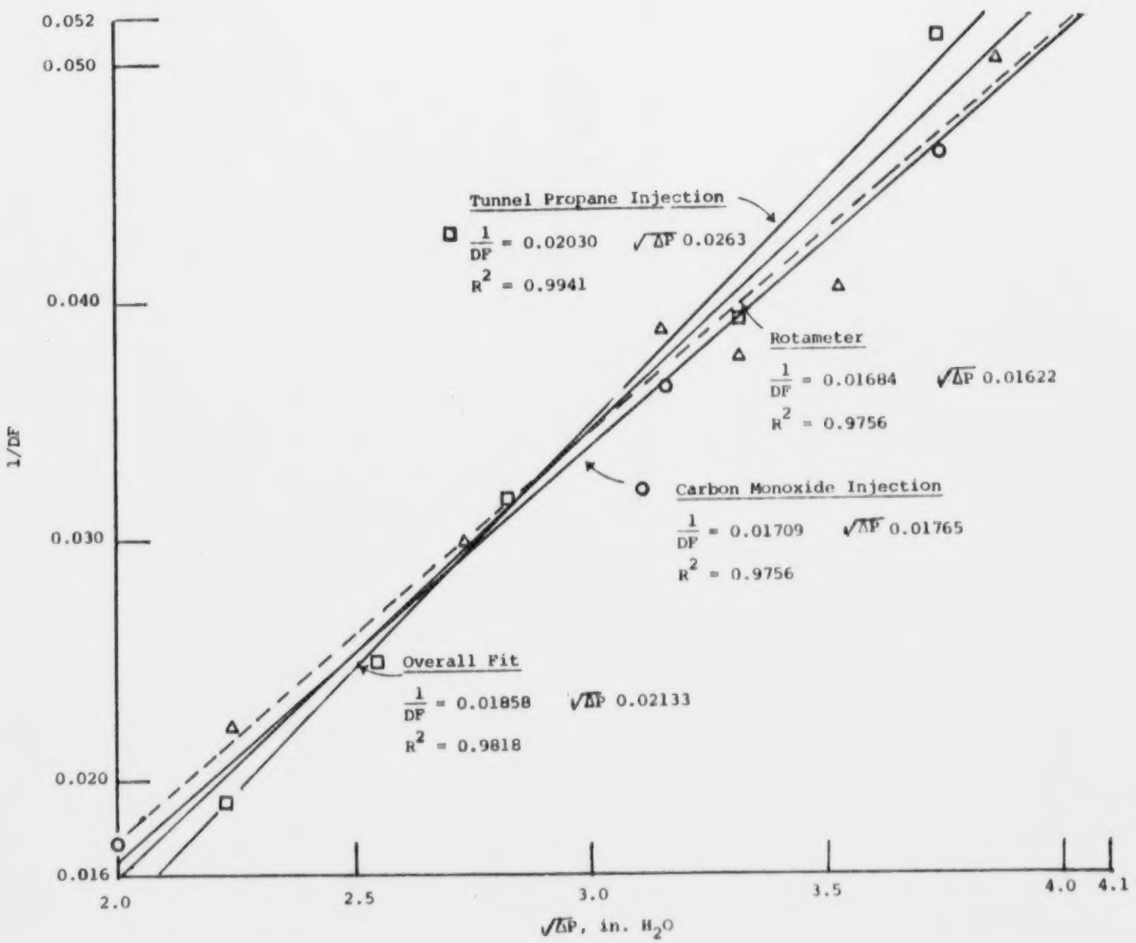


Figure 2, Calibration of N_2 secondary diluter, February 10, 1976 (least square lines).

TABLE 1. N_2 SECONDARY DILUTER CALIBRATION VALUES
FEBRUARY 10, 1976

$\sqrt{\Delta P}$	1/DF Carbon Monoxide	1/DF Propane	1/DF Rotometer
2.0	0.01712		
2.236	-------	0.01908	0.02116
2.5495	0.02500	-------	-------
2.7386	-------	-------	0.03001
2.8284	-------	0.03175	-------
3.1623	0.03650	-------	0.03882
3.3166	-------	0.03937	-------
3.5355	-------	-------	0.04062
3.7417	0.04651	0.05110	-------
3.87298	-------	-------	0.05013
4.12311	-------	0.05701	-------

	$1/DF = A(\sqrt{\Delta P}) + B$			Overall Data
A	0.01709	0.02030	0.01684	0.01858
B	-0.01765	-0.02630	-0.01622	-0.02133
R^2	0.99749	0.99414	0.97560	0.0818
(2)	0.01653	0.01430	0.01747	0.01584
(4)	0.05071	0.05491	0.05115	0.05301

PROCEDURE USED BY SwRI FOR OBTAINING DMNA TRAPS

PREPARATION OF RUNNING

1. Turn on 4 rheostats in back of DMNA cart at least 30 minutes prior to test.

2. Remove trap holder with the filter case from the cart. Insert filter (FA) into filter case so that flow goes through the dull side of the filter (note direction of arrow). Replace o-ring. The filter and the o-ring are not to be handled with bare hands. Fasten trap holder back onto cart and tighten nut.

3. Check nitrogen (N_2) bottle to make sure it has at least 1000 psi. If necessary, N_2 flow can be set with a dummy filter with the pump on. Check dryer on N_2 bottle and replace molecular sieve and silica gel dryer if necessary.

4. Open the green valve on the sample line.

READY TO RUN

1. Obtain trap from refrigerator. Leave it in the glass tube until ready to use. With disposable gloves, place trap in holder. Hand tighten both end fittings. Replace spun glass ball in glass container and recap.

2. Just prior to start of test, turn on N_2 flow. At honk of horn, turn on sample pump and set the large N_2 flowmeter with the top of the float at 65 and the magnehelic at 25" H_2O. Both knobs need to be adjusted simultaneously since they are dependent on each other. These two will have to be monitored throughout the test. Flowmeters 1, 2, and 3 should already be adjusted to their proper settings (10, 5.2, 10 respectively). If not, use the large black knobs to readjust. Temperature of the system is monitored at four points: sample inlet from CVS, N_2 inlet, mixing point and at trap. It should be set at 60°C (140°F) by adjusting rheostats in back of cart. These temperatures are recorded on the data sheet about once a week.

END OF TEST

The traps are run the full cold FTP and then the hot 505. During the soak between FTP's, the pump and the N_2 bottle are shut off.

1. When the test is over, the trap is again carefully handled with gloves and placed back in the glass container. The container is labeled on the cap and on the side of the trap number (from log book), test number and run date. The container is then placed in the 1-gallon can in the refrigerator. Test number and run date are recorded in the log book. Test number is also recorded on the data sheet (same one temperatures were recorded on).

2. Close green flow valve on sample line.

3. Turn off N_2 regulator.

4. Turn rheostats off.

APPENDIX M

DMNA ANALYSIS PROCEDURE

THE MEASUREMENT OF DMNA IN EXHAUST

As used by

Research Triangle Institute
Research Triangle Park, N.C.

Developed by

Research Triangle Institute
Research Triangle Park, N.C.

November 1978

RESEARCH TRIANGLE INSTITUTE

ANALYSIS FOR N-NITROSODIMETHYLAMINE IN EXHAUST GASES USING A TENAX GS CARTRIDGE AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY/COMPUTER

EPA Contract No. 68-02-2767

RTI/1514/00-01S

Special Interim Technical Report

by

E. D. Pellizzari, Project Director

Date: November 27, 1978

Project Officer
Ron Bradow
Mobile Source Emissions Reserach Branch
Mail Drop 46, ERC Annex
U.S. Environmental Protection Agency
Research Triangle Park, N. C. 27709

Prepared for the Environmental Protection Agency, Reserach Triangle Park, N. C. 27711

RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

The information presented in this document is subject to the following qualifications:

(a) The mention of a specific company does not imply the intent to regulate that company or its activities nor that, unless specifically stated, the company is the source of a given compound;

(b) The identification of compounds were determined by mass spectrometric and retention index techniques and their identity are subject to the limits of this methodology.

(c) The mention of compounds in this report does not imply that they are necessarily carcinogenic or mutagenic;

(d) The possible mutagenic or carcinogenic activity attributed to a compound is based upon cited literature;

and (e) The experimental findings and conclusion presented in this report should not be cited, reproduced, or included in other publications without the expressed approval of the Project Director or Officer.

1.0 Introduction

Because of the previous reports of the presence of N-Nitrosodimethylamine in ambient air, interest in the determination of DMN in auto exhaust heightened. N-Nitrosodimethylamine (DMN) levels in ambient air were determined for an area surrounding an industrial site in Baltimore, Maryland. Using Tenax GC cartridge for concentrating DMN and glass capillary/glass-liquid chromatography/mass spectrometery with specific ion (m/z 74) monitoring, DMN was detected and quantified. On an industrial site DMN levels reached 32,000 ng/cm (10.67 parts per billion) in the ambient air.

On the basis of these and other observations, research was conducted on determineing whether N-nitrosodimethylamine was present in auto exhaust. In conjuction with Southwest Research Institute, a study was conducted on the detection of DMN in auto exhaust of automobiles which have been operated under various test conditions. SwRI was responsible for generating and participating in the collection of the auto exhaust samples during the course of this program. The results of this research effort is described here.

2.0 Experimental Procedures

The collection and analysis techniques given in Appendix A were modified and used for detecting DMN in auto exhaust gases.

Tenax GC sampling cartridges were prepared at the Research Triangle Institute (RTI) and shipped by Federal Express to Southwest Research Institute (SwRI) for the collection of auto exhaust samples and subsequent returned to RTI for analysis. In all cases the sampling cartridges were expended or returned within four to five weeks and replaced with a fresh batch in order to insure a low background level. All samples were analyzed within two to three weeks after sample collection was completed.

The sampling procedure employed by SwRI consisted of a primary and secondary diluter and the secondary diluter and transfer lines were maintained at 60°C. The sampling rate was 1.6 ℓ/min and the test length was approximately 31 minutes giving a total sample volume of 50 ℓ. The average primary cvs dilution was 11.1 to 1 and the secondary dilution was 16.7 to 1 giving an actual sample dilution of 185 to 1. The secondary diluter was necessary in order to insure that the NO_x and hydrocarbon values were at levels which minimized the potential artifact formation of the N-nitrosodimethylamine on the Tenax GC sorbent.

(APPENDIX A)

N-NITROSODIMETHYLAMINE IN AMBIENT AIR
ANALYTICAL METHOD

Analyte:	DMN	Method No:	
Matrix:	Air	Range:	0.5 ppt - 10 ppb
Procedure:	Adsorption on Tenax GC, thermal desorption with He purge, measurement by capillary gas-liquid chromatography/ mass spectrometry	Precision:	±10%
Date Issued:		Classification:	E (Proposed)
Date Revised:			

---

1. Principle of Method

N-nitrosodimetnylamine (DMN) is concentrated from ambient air on Tenax GC in a short glass tube (1,2). It is desorbed by heating and purging with helium into a liquid nitrogen cooled nickel capillary trap and then introduced onto a high resolution gas chromatographic column where is is separated from interferences. The concentration of DMN is measured from the mass spectrometric signal at m/e 74 (3).

2. Range and Sensitivity

2.1 The range of the mass spectrometric signal for the conditions listed corresponds to 0.5 ppt to 10 ppb.

2.2 A concentration of 0.5 ppt of DMN can be determined in a 150-liter air sample.

3. Interferences

Interferences may result from materials having background ions of m/e 74 ($C_2H_8N_3$, $C_2H_4NO_2$, $C_2H_6N_2O$, C_3H_3Cl, C_3H_6S, $C_3H_6O_2$, or $C_3H_{10}N_2$), if at the same retention time of DMN.

4. Precision and Accuracy

4.1 The precision of this method has been determined to be ±10% or relative standard deviation when replicate sampling cartridges were spiked with 50 ng (corresponding to 10 ppb in 150 ℓ of air). These data were obtained using 10.0 cm long glass tubes (1.5 cm i.d.)packed with 35/60 mesh of Tenax GC (bed dimensions: 1.5 cm x 6 cm in depth).

4.2 The accuracy of the analysis is approximately ±10% of the amount reported as determined from repeated analysis of several standards.

5. Advantages and Disadvantages of the Method

5.1 The gas chromatography-mass spectrometry technique interfaced with a Finnigan glass jet separator (Model 01512-42158 Finnigan Corp., Sunnyvale, CA) is extremely sensitive and specific for the analysis of DMN. The high resolution gas chromatographic separation yields a retention time that is characteristic for DMN, and relatively specific for positive assignment of the signal as DMN. The mass spectrometer in combination with high resolution gas chromatography yields a very high degree of specificity. The base peak of DMN is at *m/e* 74 which is also the parent ion. In order to assign the signal at *m/e* 74 to DMN it is absolutely necessary that the retention time matches with the signal.

5.2 Collected samples can be stored up to 1 month with less than 10% losses.

5.3 Because DMN is a suspected carcinogen in man it is extremely important to exercise safety precautions in the preparation and disposal of liquid and gas standards, cleaning of used glassware, etc., and the analysis of air samples.

5.4 Since the mass spectrometer can not be conveniently mobilized sampling must be carried out away from the instrument.

5.5 High resolution gas chromatography/low resolution mass spectrometry is not a convenient technique for handling a large number of samples (>100/wk).

5.6 Efficiency of air sampling increases as the ambient air temperature decreases (*i.e.* sensitivity increases).

5.7 Ambient air sampling is limited to cases where the NO_x levels are less than 3 ppm when dimethylamine is also present.

6. Apparatus

6.1 Sampling Tubes

6.1.1 The sampling tubes are prepared by packing a 10 cm long x 1.5 cm i.d. glass tube with 6.0 cm of 35/60 mesh Tenax GC with glass wool in the ends. Cartridge samplers are conditioned at 270°C with helium flow at 30 mℓ/min for 20 min. The conditioned cartridges are transferred to Kimax® (2.5 cm x 150 cm) culture tubes, immediately sealed using Teflon-lined caps, and cooled.

6.1.2 Cartridge samplers with longer beds of sorbent may be prepared using a proportional amount of Tenax GC.

6.2 Gas Chromatographic Column

6.2.1 A 0.35 mm i.d. x 50 m glass SCOT capillary coated with DEGS stationary phase and 0.1% benzyl triphenylphosphonium chloride is used. The capillary column is conditioned (detector end disconnected) for 48 hr at 210°C @ 1.5-2.0 mℓ/min helium flow.

6.3 A Finnigan type glass jet separator on a magnetic or quadropole instrument is used at 200°C.

6.4 Inlet-Manifold

6.4.1 An inlet-manifold is fabricated and employed (Fiugre 1, ref, 1,2,4).

6.5 Gas Chromatograph

6.5.1 A Varian 1700 gas chromatograph or equivalent. A gas chromatograph employing a single column oven and a temperature programmer is adequate.

6.6 Mass Spectrometer

6.6.1 A mass spectrometer with a resolution of 500-2000 equipped with single ion monitoring capabilities must be used in conjunction with a gas chromatograph. A Varian-MAT CH-7 has been found to be satisfactory for this purpose (2,3).

6.7 Syringes

6.7.1 Syringes, 1-mℓ gas tight (Precision Sampling, Inc.) and 10 μℓ (The Hamilton Co., Inc.).

7. Reagents and Materials

All reagents must be analytical reagent grade.

7.1 N-nitrosodimethylamine

7.2 Acetone

7.3 Isoclean®

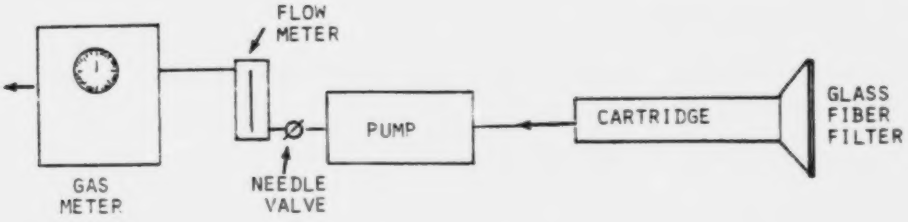
7.4 Tenax GC (35/60 mesh, Applied Science)

7.5 Two 2-liter round bottom flasks fitted with injection ports.

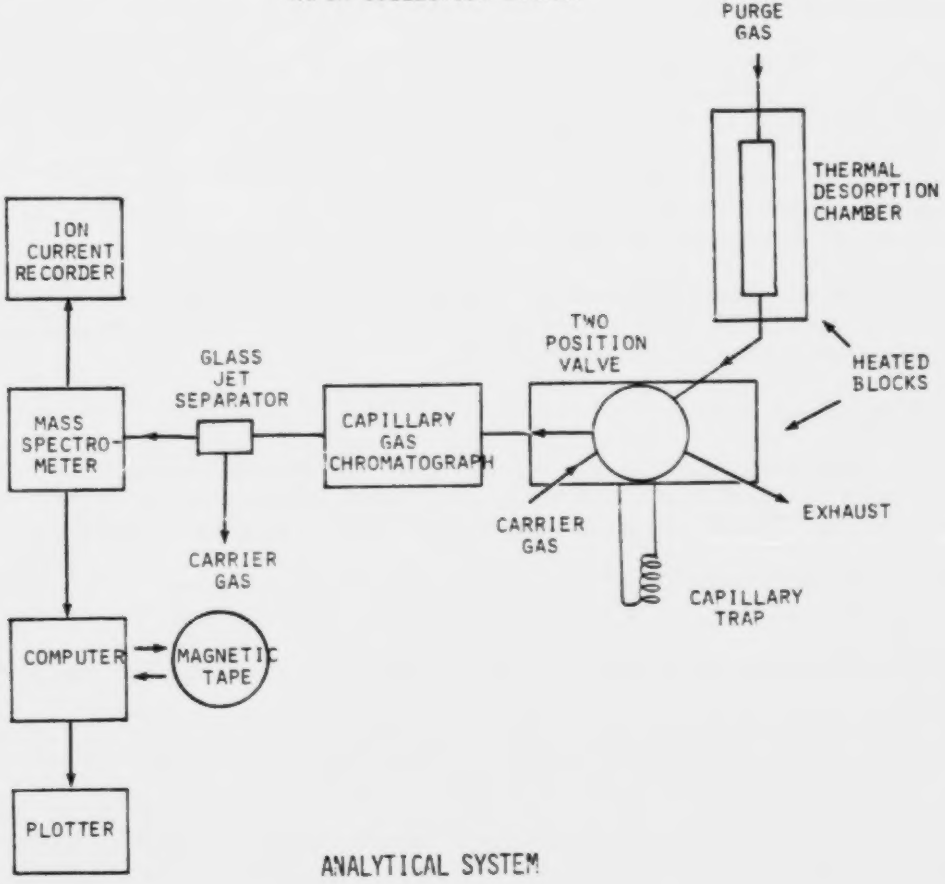
7.6 Soxhlet apparatus

8. Procedure

8.1 Cleaning of glassware


FLOW METER
GAS METER
NEEDLE VALVE
PUMP
CARTRIDGE
GLASS FIBER FILTER

VAPOR COLLECTION SYSTEM


PURGE GAS
THERMAL DESORPTION CHAMBER
ION CURRENT RECORDER
TWO POSITION VALVE
HEATED BLOCKS
GLASS JET SEPARATOR
MASS SPECTROMETER
CAPILLARY GAS CHROMATOGRAPH
EXHAUST
CARRIER GAS
CARRIER GAS
CAPILLARY TRAP
COMPUTER
MAGNETIC TAPE
PLOTTER

ANALYTICAL SYSTEM

Figure 1. Vapor collection and analytical systems for analysis of hazardous vapors in ambient air.

All glassware, glass sampling tubes, cartridge holders, etc. should be washed in Isoclean®/water, rinsed with doubly distilled water and acetone and air dried. Glassware is heated to 450°F for 2 hrs.

8.2 Preparation of Tenax GC

8.2.1 Virgin Tenax GC is extracted in a Soxhlet apparatus overnight with acetone prior to its use.

8.3 Collection of DMN in Ambient Air

8.3.1 Continuous sampling of ambient air may be accomplished using a Nutech Model 221-A portable sampler (Nutec Corp., Durham, NC) or its equivalent (2). Flow rates are adjusted with a metering valve through a calibrated rotameter. Total flow is registered by a dry gas meter.

8.3.2 For larger sample sizes it is important to realize that a larger total volume of air may cause elution of DMN through the sampling tube. It has been demonstrated that exceeding a total of 385, 332, 280, 242, 224, 204, 163, 156, 148, 127, 107, 93, or 79-liters of air at temperatures of 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105 or 110°F, respectively will result in elution of DMN from the cartridge sampler. A flow of 10 cc/min to 30 ℓ/min may be used with the sampler described in 6.1.

8.3.3 DMN has been found to be stable and quantitatively recoverable from cartridge samplers after 4 weeks when tightly closed in cartridge holders, protected from light and stored at 0°C.

8.4 Analysis of Sample

8.4.1 Instrument Conditions and Set-up. The thermal desorption chamber and six-port valve are set to 200°C. The glass jet separator is maintained at 200°C. The mass spectrometer is set to monitor m/e 74 (Figure 2).

8.4.2 Adjust the He purge through the desorption chamber to 50 mℓ/min. Cool the Ni capillary trap at the inlet manifold with liquid nitrogen.

8.4.3 Place the cartridge sampler in the desorption chamber and desorb for 5 min.

8.4.4 Rotate the six-port valve on the inlet-manifold to position "B", heat the Ni capillary trap to 180°C with a wax bath.

8.4.5 Temperature program the glass capillary column from 75 to 205°C at 4°C/min and hold at upper limit for 10 min. The retention time of DMN is approximately 26 min (Figure 3).

8.4.6 The analytical column is cooled to ambient temperature and the next sample is processed.

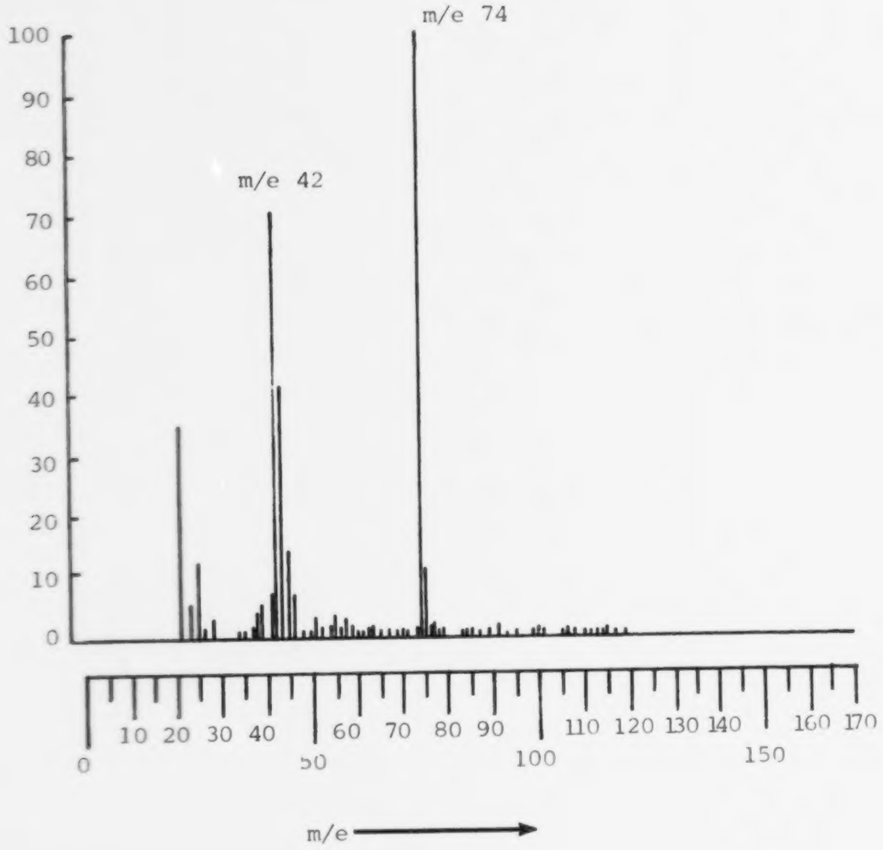


Figure 2. Mass spectrum of N-nitrosodimethylamine.

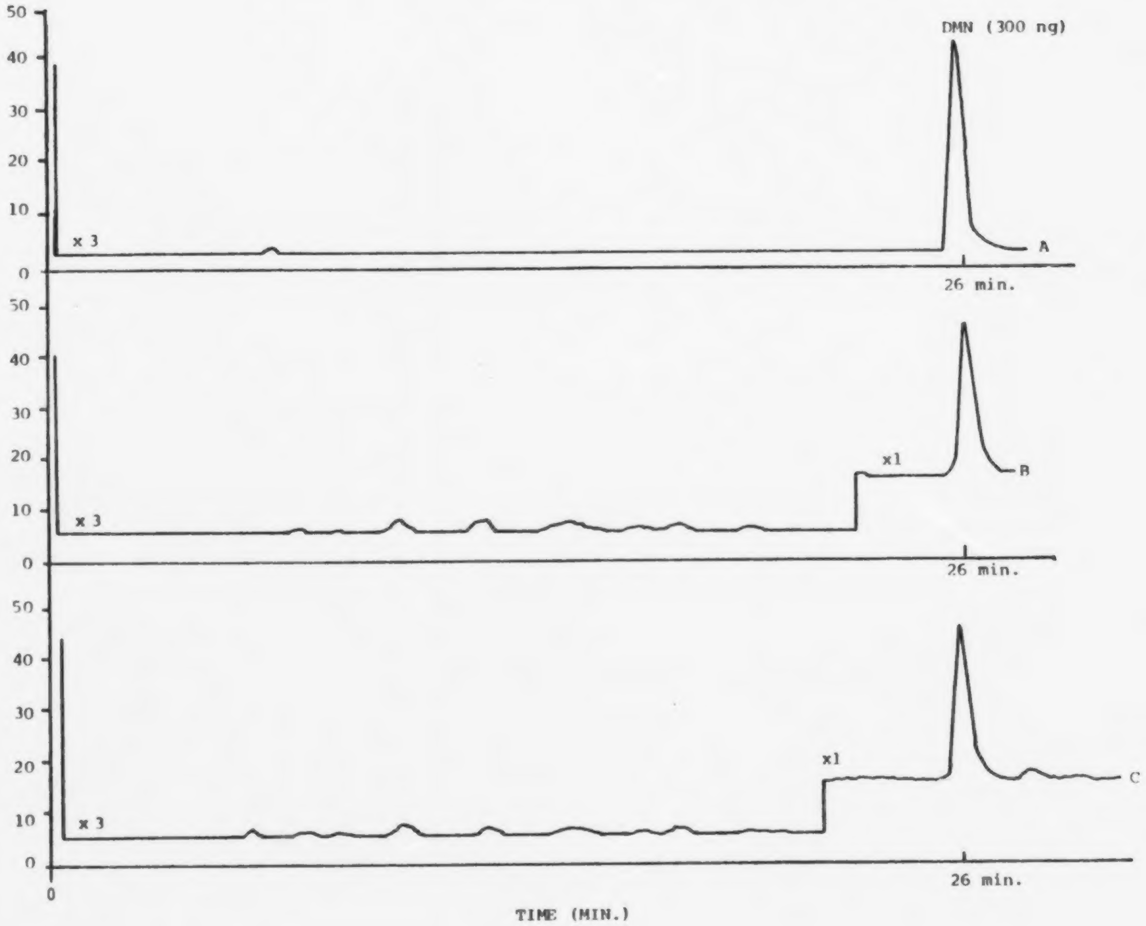


Figure 3. Mass (m/e 74) Chromatograms. A = standard DMN, B,C = replicate air samples.

9. Calibration and Standards

9.1 Preparation of Gas Standard

9.1.1 Purge two-2 liter round bottom flask with helium, warm flasks to 50°C with heating mantels and use magnetic bar to stir vapors.

9.1.2 Inject 0.1-1 μℓ of DMN into flask and let stir for 30 min. Make further dilutions into second flask by transferring milliliter gas volumes as needed.

9.1.3 Purge air/vapor mixtures from second flask onto cartridge samplers.

9.2 Calibration

9.1.2 Prepare standard curve (with ten concentration points) by thermally desorbing cartridge samplers loaded with 3 ng to 30 μℓ of DMN. Plot m/e 74 response vs ng of DMN. A linear response is observed.

10. Calculations

10.1 The total quantity of DMN in ambient air is determined by comparting m/e 74 response for samples of DMN with standard curve.

$$\text{ppb} = \frac{\text{ng DMN}}{\text{V}} = \frac{24.45}{74}$$

where:

ng DMN = total ng concentration is determined in 9.2.1

V = volume of air in liters sampled at 25°C and 760 torr

24.45 = molar volume of an ideal gas at 25°C and 760 torr

MW = moleculat weight of DMN, 74.

11. References

1. Pellizzari, E. Development of Method for Carcinogenic Vapor Analysis in Ambient Atmosphere, Pub. No. EPA-650/2-74-121, 1974. 148 pp.

2. Pellizzari, E. Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors. Pub. No. EPA-600/2-75-076, 1975, 187 pp.

3. Pellazzari, E., J.E. Bunch, R.E. Berkley and J. McCrae, Biomedical Mass Spec, submitted.

4. Pellizzari, E.D., B.H. Carpenter, J.E. Bunch, and E. Sawicki, Environ. Sci. Tech., 9, 556 (1975).

APPENDIX N

BaP SAMPLING AND ANALYSIS

SAMPLING AND ANALYSIS OF BaP

Sample Collection at
Southwest Research Institute

Analysis Method Developed and used at

Environmental Protection Agency
Research Triangle Park, N.C.

June 1979

SAMPLING AND ANALYSIS OF BENZO-α-PYRENE

The analysis for benzo-α-pyrene (BaP) will be carried out by collecting particulate samples on 8" x 10" glass fiber filters at Southwest Research Institute and sending the filters to EPA-Research Triangle Park for analysis by fluorscence spectroscopy.*

Sampling for BaP has been successfully conducted in the past at Southwest Research by collecting diesel particulate on 8" x 10" glass fiber filters. Other filtering media and/or sizes are under consideration for sampling and may be used in the future. Sample flow rates will depend on filter size and loading capacity. The temperature of the dilute exhaust at the sampling point will not exceed 125°F.

After the filters have been loaded with sample they will be weighed, folded in half so that the particulates are inside and folded again. All samples will be handled under yellow light as BaP is degraded in the presence of white light. The filter will then be placed in a glassive envelope and then in a manila envelope. Several envelopes will be placed in a ziplock plastic bag purged with zero nitrogen and heat sealed. The samples will be stored at -30°C until shipped in an insulated container with dry ice via air freight to EPA-RTP for analysis.

At EPA-RTP particles on the glass fiber filters are extracted with methylene chloride. A portion of the methylene chloride solution is analyzed for BaP. The methylene chloride solution is diluted with cyclohexane and spotted on thin layer acetylated cellulose plates. The plates are developed and the fluorescence due to BaP is measured in a spectrophotometer. The concentration of BaP is determined by comparing the response of the sample to the response of a series of standards.

---

* Private communication with EPA-RTP.

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA-335

U.S. MAIL

Official Business
Penalty for Private Use $300

Please make all necessary changes on the above label, detach or copy, and return to the address in the upper left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐; detach, or copy this cover, and return to the address in the upper left-hand corner.

EPA-600/2-80-068

B96/9